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(71)Applicant : ASAHI CHEM IND CO LTD

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(72)Inventor : MATSUSHITA FUMIO
NOZAKI TAKASHI
YAMAGUCHI FUMIHIKO

(54) PRODUCTION OF POLYOLEFIN

(57)Abstract:

PURPOSE: To obtain an olefinic polymer capable of controlling each structural level of molecular structure, micro structure, a macro structure, etc., of a polymer and having an excellent physical properties.

CONSTITUTION: This method for producing a polyolefin comprises carrying out the first stage polymerization in multistage polymerization using a catalyst for an olefine polymerization comprising [A] a transition metal compound of a group IVB containing a ligand having a cyclopentadienyl skeleton and [B] an inorganic solid component obtained by supporting an organoaluminum compound on a fine-particle inorganic solid having hydroxyl group on the surface and as necessary, [C] an organoaluminum compound and further adding a similar compound different from a compound of the group IVB containing the ligand having cyclopentadienyl skeleton added in the first stage polymerization to the polymerization stage in at least one polymerization stage among the second or more stages thereto and carrying out polymerization of olefin.

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CLAIMS

[Claim(s)]

[Claim 1] At least two sorts of [A] cyclopentadienyl frames In case a multistage polymerization is performed using the catalyst for olefin polymerization which consists of a transition-metals compound of the IVB group containing the ligand which it has, and an inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle-like inorganic solid-state which has a hydroxyl group on the [B] (b-1) front face It sets in at least one polymerization stage among the polymerization stages after the 2nd step. The cyclopentadienyl frame added to the 1st step The manufacture approach of the olefin system polymer characterized by newly adding the transition-metals compound of the IVB group containing the ligand which has at least one sort of different cyclopentadienyl frames from the transition-metals compound of the IVB group containing the ligand which it has, and performing a polymerization.

[Claim 2] At least two sorts of [A] cyclopentadienyl frames The ligand which it has In case a multistage polymerization is performed using the catalyst for olefin polymerization which consists of an IVB group's included transition-metals compound, an inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle-like inorganic solid-state which has a hydroxyl group on the [B] (b-1) front face, and a [C] organoaluminium compound It sets in at least one polymerization stage among the polymerization stages after the 2nd step. The cyclopentadienyl frame added to the 1st step The manufacture approach of the olefin system polymer characterized by newly adding the transition-metals compound of the IVB group containing the ligand which has at least one sort of different cyclopentadienyl frames from the transition-metals compound of the IVB group containing the ligand which it has, and performing a polymerization.

[Claim 3] The manufacture approach of the olefin system polymer according to claim 1 or 2 which is an IVB group's transition-metals compound with which [A] transition-metals compound contains the ligand which has a hydrocarbon substituent cyclopentadienyl group in said polymerization catalyst.

[Claim 4] The manufacture approach according to claim 1, 2, or 3 that an olefin system polymer is an ethylene homopolymer or a copolymer of ethylene and other alpha olefins.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the olefin system polymer which has the outstanding physical properties, and its polymer. In more detail The approach and multistage polymerization method using the catalyst which consists of an inorganic solid-state component which supported the transition-metals compound and the organic aluminum oxy compound, and the polymerization method using at least two sorts of transition-metals compounds Combination, It is related with the polymer obtained by this manufacture approach about the approach of manufacturing the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, by performing structure control on each structure level, such as the molecular structure of a polymer, a microstructure, and macrostructure.

[0002]

[Description of the Prior Art] As a catalyst for manufacturing the polymer of an olefin from the former, the so-called Ziegler Natta catalyst which consists of a titanium compound and an organoaluminium compound is known. By using the catalyst which consists ethylene or ethylene, and other 1-olefins of alumoxane which is one sort of the halogen content transition-metals compound of fusibility, such as screw (cyclopentadienyl) zirconium dichloride, and an organic aluminum oxy compound in polymerization activity high on the other hand in recent years, the technique which carries out a polymerization in high activity was found out, and it became well-known at JP,58-19309,A.

[0003] as the usage of a catalyst system which furthermore consist of the above-mentioned transition metals compound and an organic aluminum oxy compound, it be base on the approach depending on control of the conventional hydrogen concentration or polymerization temperature, but the method of adjust the molecular weight and the comonomer content of an olefin system polymer be also propose by JP,60-35007,A by the approach of choose the transition metals compound according to the purpose from the transition metals compounds of the varieties containing the above-mentioned transition metals compound.

[0004] Since a polymerization is possible, the polymer with narrow molecular weight distribution is further excelled also in copolymeric and the catalyst system which consists of this transition-metals compound and an organic aluminum oxy compound can obtain a polymer with many comonomer contents, and the uniform polymer of comonomer distribution compared with the so-called Ziegler Natta catalyst, it has the description that the polymer which has the physical properties which were excellent in shock resistance, solvent resistance, etc. can be obtained.

[0005] However, the advance of the latest industry is remarkable, and by the time a rise of the expectation for the polyolefine from the standpoint of an environmental problem fully fills this military requirement only with the military requirement to polyolefine only using conjointly extensive and the catalyst system which has a high level and consists of the above-mentioned transition-metals compound and an organic aluminum oxy compound by leaps and bounds, it will not result, but much more improvement in the engine performance is called for strongly.

[0006] Furthermore, since this catalyst system was meltable to a solvent, when applying to a

suspension-polymerization method or a vapor-phase-polymerization method, the description of the polymer obtained was very bad, and adhered to a wall surface, an impeller, etc. of a reactor, and it had the problem that it could not be used the way things stand industrially. Moreover, that the molecular weight distribution of a polymer are narrow also had the practical big problem of causing the fall of fabrication nature by one side, although it was advantageous in order to acquire the physical properties which were excellent like the above. The present condition is that the catalyst system which consists of a transition-metals compound and an organic aluminum oxy compound has not resulted in the full-scale industrialization by the suspension-polymerization method and the vapor-phase-polymerization method in addition now because of these problems.

[0007] Therefore, development of the polymerization method using the catalyst system containing the transition-metals compound performed so far and an organic aluminum oxy compound put [rather than] weight on the above-mentioned problem solvings, such as an improvement of the shape of polymerization somatic, and an improvement of fabrication nature, rather aiming at much more improvement in polymer physical properties. For example, in order that the description of a polymer may solve the problem of being very bad, the attempt which porous inorganic oxides, such as a silica, an alumina, and a silica alumina, are made to support one [at least] component of a transition-metals compound and an organic aluminum oxy compound, and uses it for olefin polymerization is made.

[0008] Moreover, the approach using the multistage polymerization method which is a well-known technique as an approach of improving fabrication nature is proposed. For example, in JP,3-234717,A, the method of improving the melting property of a polymer is indicated by the multistage polymerization method using the catalyst for olefin polymerization which consists of the above-mentioned transition-metals compound and an organic aluminum oxy compound. Moreover, the approach of mixing and using at least two sorts of transition-metals compounds as other means to improve fabrication nature, and making molecular weight distribution large is proposed by JP,60-35008,A. It is also collectively indicated by JP,60-35008,A that a transition-metals compound can be supported to porous inorganic support, such as a silica, an alumina, and a silica alumina.

[0009] Furthermore, for JP,5-155932,A and JP,5-155933,A, the particle-like support which has at least two or more sorts of transition-metals compounds, the amount of water of adsorption of the specific range, and the amount of a surface water acid radical is used, precuring is performed to them, and the method of improving physical properties, such as the shape of the melting tension of an olefin system polymer and corpuscular character, and improving fabrication nature is indicated.

[0010] Each these conventional approach aimed at improvement in fabrication nature, and was far from a viewpoint of much more improvement in polymer physical properties. Moreover, about the improvement of fabrication nature itself, although the conventional approach showed a certain amount of improvement effect, it was not necessarily able to be said to be enough. for example, by the multistage polymerization method, acquiring desired molecular weight distribution only by control of polymerization conditions has constraint, and by the approach using at least two sorts of transition-metals compounds It is difficult to find out the combination of a transition-metals compound suitable in order to acquire desired molecular weight distribution as a matter of fact. It is general to need costs and an effort great by it, even if it is able to find out the combination of such a transition-metals compound. The transition-metals compound moreover found out was a special compound, and also when very expensive, there was a not few problem and it was not practical.

[0011] On the other hand, the manufacturing method of the reaction blend using at least two sorts of transition-metals compounds is proposed in JP,5-310831,A. The approach using two or more reactors is also illustrated by JP,5-310831,A as a mixed means.

[0012]

[Problem(s) to be Solved by the Invention] However, it is premised on using the catalyst which all supported the transition-metals compound in the conventional approach when applying to a suspension-polymerization method or a vapor-phase-polymerization method. When performing a

multistage polymerization based on this approach, even if it newly adds the transition-metals compound supported with the latter polymerization. Since the polymer by which a polymerization is carried out with the transition-metals compound added in the latter part, and the polymer by which a polymerization is carried out with the transition-metals compound which came from the preceding paragraph turn into a polymer of ***** another kind which are [distribution / molecular weight, / presentation] different according to each catalyst. In order for the polymer of these another kind to generate independently for every support with which each catalyst was supported, therefore to grow up to be the particle of the polymer of these another kind, respectively, It became the same thing as having mixed the particles of the polymer of these another kind as a matter of fact, therefore there was a problem [polymers] that it was difficult the uniform sea island structure for every presentation unit and to go back to the microstructure in crystal level further, and to mix to homogeneity as a matter of fact.

[0013] For this reason, in case a multistage polymerization is performed, even if it adds a new transition-metals compound at a latter polymerization process based on the conventional technique and performs a polymerization. The same thing as the mixture of mere polymer powder is obtained. In being severe in not accepting a practical merit in the physical properties of a polymer at all an uneven presentation distribution of the obtained polymer sake -- the fall of a mechanical strength, generating of gel, etc. -- good -- since it was better, colander evil was also generated, and practical use was not able to be presented.

[0014] And if a multistage polymerization method and the approach using at least two sorts of transition-metals compounds are applied. For example, the structure control with molecular levels, such as a molecular weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, Control of microstructures, such as a distributed condition in crystal size, crystallinity, and crystal level, Furthermore, things for which each structure is controlled the optimal in each structure level of a polymer, such as control of macrostructures, such as sea island structure for every presentation unit, become possible. There were a purport which can manufacture the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, and no example indicated concretely. Rather than it applies the describing [above] multistage polymerization method and the approach using at least two sorts of transition-metals compounds furthermore, as a concrete example. For example, although it becomes possible to control molecular weight distribution in the easy and broad range by adopting the polymerization conditions on which a different new transition-metals compound from the transition-metals compound used for the polymerization of the preceding paragraph is added, and polymerization conditions also differ from the polymerization conditions of the preceding paragraph in case a latter polymerization is performed. The indication of such an example was not seen at all conventionally.

[0015] This invention offers the polymer obtained by the manufacture approach of the olefin system polymer substantially mixed with homogeneity, and its approach. Furthermore, molecular weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, Distribution of the structure control with molecular levels, such as the mixed state of molecules, crystal size, and this crystal size, Further control of macrostructures, such as sea island structure for every presentation unit, etc. control of microstructures, such as a distributed condition in crystallinity and crystal level, and by controlling each structure the optimal in each structure level of a polymer. It aims at offering the polymer obtained by the method of manufacturing the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, and its approach.

[0016]
[Means for Solving the Problem] In the catalyst system which this invention persons become from a transition-metals compound and an organic aluminum oxy compound. The result of having repeated research wholeheartedly in order to aim at improvement in physical properties of the polymer obtained, If the approach and multistage polymerization method using the catalyst which consists of an organic aluminum component if needed [the inorganic solid-state component and if needed] which supported the transition-metals compound and the organic aluminum oxy compound, and the polymerization method using at least two sorts of transition-metals

compounds are combined Control on each structures level, such as the molecular structure of a polymer, a microstructure, and macrostructure, is possible. By optimizing structure in each structure level, a synergistic effect is discovered and it came to make a header and this invention for the olefin system polymer which has the surprising engine performance which was not able to be obtained at all being obtained with the conventional technique.

[0017] This invention At least two sorts of [A] cyclopentadienyl frames The catalyst for olefin polymerization which will serve as a transition-metals compound of the IVB group containing the ligand which it has, and an inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle-like inorganic solid-state which has a hydroxyl group on the [B] (b-1) front face from the [C] organoaluminium compound if required is used. Furthermore, it sets in at least one polymerization stage among the polymerization stages after the 2nd step using a multistage polymerization in the case of this multistage polymerization. By newly adding the transition-metals compound of the IVB group containing the ligand which has at least one sort of different cyclopentadienyl frames from the transition-metals compound of the IVB group containing the ligand which has the cyclopentadienyl frame added to the 1st step, and performing a polymerization, the molecular structure of a polymer, The approach of manufacturing the olefin system polymer which controls each structures level, such as a microstructure and macrostructure, and has the outstanding physical properties is offered, and the polymer obtained by this manufacture approach is offered.

[0018] Hereafter, the olefin system polymer by which a polymerization is carried out by the multistage polymerization method and this approach of the olefin concerning this invention is indicated concretely. In addition, in this invention, it may be used with a "polymerization" in the semantics which included not only homopolymerization but copolymerization, and may be used with a "polymer" in the semantics which included not only a homopolymer but the copolymer.

[0019] When olefin polymerization is performed by this invention using the catalyst for olefin polymerization which will serve as [A] transition-metals compound and [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle (b-1)-like inorganic solid-state from the [C] organoaluminium compound if required, [A] In order that a transition-metals compound and the organic (b-2) aluminum oxy compound supported on [B] inorganic solid-state component may form the polymerization active spot, A polymer is generated on [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported, and [B] inorganic solid-state component grows up to be a polymer particle as a result. If two or more sorts of [A] transition-metals compounds exist in a polymerization system in the case of a polymerization, two kinds of polymers will generate according to [** A] transition-metals compound. In this case, in order to generate the polymer of these two classes on the same [B] inorganic solid-state component at coincidence, the polymer particle to which two kinds of polymers were substantially mixed with homogeneity with the molecular level as a result is obtained. Thus, it became possible to manufacture the polymer considered that it cannot be at all conventionally as a result of mixing two kinds of polymers with homogeneity with a molecular level substantially. For example, mixing with the ethylene polymer of the amount of giant molecules and the ethylene polymer of low molecular weight was not mixed with homogeneity if the ethylene polymer which has the molecular weight of the interstitial segment of this amount part of giant molecules and a low-molecular-weight part did not exist, but it caused the fall of a mechanical strength, and generating of gel, and has been considered that it cannot mix and use it at all. However, it became possible to mix the amount ethylene polymer of giant molecules, and a low-molecular-weight ethylene polymer with a direct molecular level, without making the ethylene polymer which has the molecular weight of this interstitial segment exist, when using the approach of this invention.

[0020] It depends on coordination force, polymerization activity, etc. over the organic aluminum oxy compound of a transition-metals compound for the mixed ratio of two kinds of polymers which are this invention, for example, are generated when making two sorts of transition-metals compounds live together in one polymerization stage and carrying out the polymerization of the mixture of a polymer. By following, for example, choosing a suitable transition-metals compound in the example of mixing of the above-mentioned amount ethylene polymer of giant molecules,

and a low-molecular-weight ethylene polymer, it is possible to control the quantitative ratio of the amount part of giant molecules of an ethylene polymer and a low-molecular-weight part, therefore if this technique is used, a polymerization is possible for the ethylene polymer which has a desired molecular weight distribution. Thus, it is possible to control a polymer by this invention with a molecular level.

[0021] The polymerization of the polymer with which two kinds of polymers were substantially mixed with the surprising thing with the molecular level is realizable even if it adds gradually two sorts of [A] transition-metals compounds. For example, when using one sort of transition-metals compounds first, performing a polymerization, adding the transition-metals compound of another kind after that and performing a polymerization, in the first polymerization, the polymer according to the transition-metals compound used first generates, and the polymer with which two kinds of polymers according to the transition-metals compound and the transition-metals compound of this another kind which were used for the beginning from the time of adding the transition-metals compound of another kind after that were mixed with homogeneity generates. The polymer obtained turns into a polymer which the polymer obtained first and the polymer with which two kinds of polymers were mixed with homogeneity were mixed, and became sea island structure as a result of such a polymerization. If the quantitative ratio of the polymer obtained first and the polymer with which two kinds of polymers were mixed with homogeneity is controlled, it will become possible to control the sea island structure of the polymer finally obtained.

[0022] Like this example, by newly adding the transition-metals compound of another kind after the first polymerization, it was what is not expected that the polymerization based on an another kind transition-metals compound arises, and it was a just surprising thing from the common sense of the conventional technique. Namely, the thing usually predicted in the example like the above From what will be covered with the polymer which the polymerization active spot formed on support generated by the first polymerization Even if it newly adds the transition-metals compound of another kind after that, the transition-metals compound of this another kind cannot contact the organic aluminum oxy compound on support. Therefore, the polymerization activity with the transition-metals compound of this another kind that could not form the polymerization active spot but was newly added is being unable to expect.

[0023] However, even if it newly adds the transition-metals compound of another kind after the first polymerization like the above-mentioned example in the catalyst system of this invention to a surprising thing, the polymerization activity based on the transition-metals compound of this another kind is discovered. Although it is thought that this has suggested the transition-metals compound of this another kind reaching to the organic aluminum oxy compound which diffused the inside of the polymer made first and was supported by the inorganic solid-state component, and forming the polymerization active spot, it is unknown for details.

[0024] By this invention, in order to expand the effectiveness of this polymerization further, a polymerization is performed by the multistage polymerization. That is, when newly adding the transition-metals compound of another kind, the polymerization conditions which differ from the first polymerization conditions by the multistage polymerization are adopted, and much more optimization of polymer structure is enabled. The multistage polymerization method as used in the field of this invention means the polymerization method which performs a polymerization gradually by letting it pass one by one to the curing units which arranged curing units in the serial and arranged the polymerization product in the middle of a catalyst component or/and a polymerization in this serial.

[0025] The catalyst for olefin polymerization which will serve as [A] transition-metals compound and [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle (b-1)-like inorganic solid-state from the [C] organoaluminium compound in the multistage polymerization of this invention if required is used. In at least one polymerization stage, at least one sort of different transition-metals compounds from the transition-metals compound added to the 1st step are newly added among the polymerization stages after the 2nd step, and a polymerization is performed. Therefore, in this invention, at least two sorts of [A] transition-metals compounds are used. Moreover, in the multistage

polymerization of this invention, a polymerization monomer besides a catalyst component, a comonomer, a solvent, etc. may be added in the polymerization stage after the 2nd step. By controlling the classes and amounts of an additive other than such a catalyst component, the width of structure control of a polymer can be extended further.

[0026] For example, at the time of the 1st step of polymerization, use the transition-metals compound which ethylene can giant-molecule quantify, perform the gay polymerization of ethylene, and the polymerization of the ultrahigh-molecular-weight ethylene polymer is carried out. If an alpha olefin is added as the transition-metals compound which was newly excellent in copolymeric with the 2nd step of polymerization, and a comonomer component and a low consistency ethylene polymer is made into a polymerization It is possible to manufacture the polymer in which the ultrahigh-molecular-weight ethylene polymer carried out micro-disperse to the polymer or low consistency ethylene polymer which was not in the former, and in which the low consistency ethylene polymer carried out micro-disperse to the ultrahigh-molecular-weight ethylene polymer. By controlling such sea island structure suitably, extrusion molding and injection molding of an ultrahigh-molecular-weight ethylene polymer impossible former absolutely become possible.

[0027] In this invention, processes which do not perform a polymerization substantially, such as a mixed process, a degasifying process, cooling, or a temperature up process, may be between the curing units located in a line with the serial. Structure control of a polymer will not be attained without the polymerization method using the catalyst system of this invention, and this. Therefore, according to the approach of this invention, manufacture of synergy polyolefine is attained.

[0028] The synergy polyolefine as used in the field of this invention means further the olefin system polymer whose physical properties improved by leaps and bounds compared with the polyolefine by the conventional technique control of microstructures, such as molecular structure control, crystal sizes and degree of crystallinity, such as molecular weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, and an array of a crystal, and by [, such as control of macrostructures, such as sea island structure for every presentation unit,] controlling each structure the optimal in each structure level of a polymer. In the combination of the physical properties that whose it was the physical properties which conflict with the conventional technique, and was made compatible in such an olefin system polymer it was made impossible, it is also possible to raise both physical properties.

[0029] Thus, it is thought that it is based on the synergistic effect by optimization on each structures level, such as the above-mentioned molecular structure, a microstructure, and macrostructure, that the physical properties which were excellent by leaps and bounds are realizable, and optimization on such each structure level becomes realizable for the first time by the approach of this invention. The improvement in fast of the physical properties in this invention means the case where 30% or more of improvement is made for example, in view physical properties etc.

[0030] As a concrete example of the above-mentioned synergy polyolefine, although the ultra high molecular weight polyethylene in which said extrusion molding and injection molding are possible is mentioned, for example, the polyethylene which has realized having the high rigidity and high shock resistance which have been considered not to coexist conventionally, and high ESCR is mentioned as other examples by carrying out micro-disperse of the low density polyethylene with uniform comonomer distribution with a narrow ($M_w/M_n=2-5$) molecular weight distribution into high density polyethylene.

[0031] As still more nearly another example, extrusion-molding nature and a die swell are improved by controlling molecular weight distribution the optimal, ESCR and shock resistance are raised by controlling the comonomer content in each molecular weight the optimal further, and the polyethylene which has realized having a moldability, high ESCR, and high shock resistance as the result is mentioned.

[0032] According to the approach of this invention, it is possible to manufacture the polyolefine which has the outstanding engine performance which was not able to be obtained at all with the conventional technique in this way. In especially an ethylene system polymer, the effectiveness

is greatest. This invention is explained still more concretely below. As a transition-metals compound of the IVB group containing the ligand which has [A] cyclopentadienyl frame used by this invention, the compound expressed with following general formula ** can be illustrated. ML_x ** [0033] the above-mentioned general formula ** -- setting -- M -- the [periodic table], although it is an IVB group's transition metals It is a zirconium, titanium, or a hafnium and L is specifically a ligand configured in transition metals. At least one L A carbon number L other than the ligand which is a ligand which has a cyclopentadienyl frame and has a cyclopentadienyl frame The hydrocarbon group of 1-12, An alkoxy group, an aryloxy radical, a halogen atom, a trialkylsilyl group, -SO₃ R (however, R is the hydrocarbon group of the carbon numbers 1-8 which may have substituents, such as a halogen.) Or it may be a hydrogen atom, or you may be a hetero 3 seat ligand, and x is the valence of transition metals.

[0034] As a ligand which has a cyclopentadienyl frame For example, a cyclopentadienyl group or a methylcyclopentadienyl radical, A dimethylcyclopentadienyl radical, a trimethylcyclopentadienyl radical, A tetramethylcyclopentadienyl radical, a pentamethylcyclopentadienyl group, An ethylcyclopentadienyl radical, a methylethyl cyclopentadienyl group, A propylcyclopentadienyl radical, a methylpropyl cyclopentadienyl group, Alkylation cyclopentadienyl groups, such as a butylcyclopentadienyl radical, a methylbutyl cyclopentadienyl group, and a hexyl cyclopentadienyl group, or an indenyl group, 4, 5 and 6, a 7-tetrahydro indenyl group, a fluorenyl group, etc. can be illustrated. The halogen atom, the trialkylsilyl group, etc. may permute these radicals, and the hetero atom which can serve as a joint seat further may permute them. Moreover, the cyclopentadienyl frame of this invention may contain the hetero atom in the frame.

[0035] Especially in the ligand configured in these transition metals, an alkylation cyclopentadienyl group is desirable. When the compound expressed with the above-mentioned general formula ** contains two or more ligands which have a cyclopentadienyl frame, the ligand which has two cyclopentadienyl frames among those may be combined through permutation silylene radicals, such as permutation alkylene group; silylene radicals, such as alkylene group; isopropylidene, such as methylene, ethylene, and a propylene, and diphenylmethylene, or a dimethyl silylene radical, a diphenyl silylene radical, and a methylphenyl silylene radical, etc.

[0036] By this invention, the following is mentioned as a more concrete example of ligands other than the ligand which has a cyclopentadienyl frame. For example, specifically, aralkyl radicals, such as aryl groups, such as cycloalkyl radical; phenyl groups, such as alkyl group; cyclopentyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, and a decyl group, a cyclohexyl radical, and a cyclo octyl radical, and a tolyl group, benzyl, and a neo fill radical, are illustrated for a carbon number as a hydrocarbon group of 1-12.

[0037] Moreover, as an alkoxy group, a methoxy group, an ethoxy radical, a butoxy radical, etc. are illustrated. A phenoxy group etc. is illustrated as an aryloxy radical. Moreover, a fluorine, chlorine, a bromine, iodine, etc. are illustrated as a halogen atom. As a ligand furthermore expressed with -SO₃ R, a p-toluene sulfonate group, a methane sulfonate group, a trifluoromethane sulfonate group, etc. are illustrated. Furthermore as a hetero 3 seat ligand, a hydronalium tris pyrazolyl borate radical, a TORISUBISU phenyl oxo-phosphoranyl radical, etc. are illustrated.

[0038] The compound expressed with the above-mentioned general formula ** is more specifically expressed with following general formula **, when the valence of transition metals is 4.

R₁ a R₂ b R₃ c R₄ d M ** (among formula **) M is a zirconium, titanium, or a hafnium and is R₁. It is the ligand which has a cyclopentadienyl frame. R₂ and R₃ And R₄ The ligand which has a cyclopentadienyl frame, it is alkyl group, cycloalkyl radical, aryl group, aralkyl radical, alkoxy group, aryloxy radical, halogen atom, trialkylsilyl group, and -SO₃ R or a hydrogen atom, and a is one or more integers and is a+b+c+d=4.

[0039] In this invention, it sets to the above-mentioned general formula **, and is R₂ and R₃. And R₄ The transition-metals compound which is the ligand in which one piece has a cyclopentadienyl frame inside, for example, R₁, And the transition-metals compound which is the ligand in which R₂ has a cyclopentadienyl frame is used preferably. The ligand which has these

cyclopentadienyl frames An alkylidene radical; silylene radical or dimethyl silylenes, such as ethylene and a propylene, [, such as alkylene group; diphenylmethylene] [, such as permutation alkylene group; isopropylidene] You may be combined through permutation silylene radicals, such as diphenyl silylene and methylphenyl silylene, etc. Moreover, R3 And R4 They are ligand [which has a cyclopentadienyl frame], alkyl group, cycloalkyl radical, aryl group, aralkyl radical, alkoxy group, aryloxy radical, halogen atom, trialkylsilyl group, and SO3 R, or a hydrogen atom.

[0040] Below, M illustrates a compound concrete about the transition-metals compound which is a zirconium. Namely, for example, screw (cyclopentadienyl) zirconium dichloride, Screw (indenyl) zirconium jib ROMIDO screw (indenyl) zirconium dichloride -- Screw (indenyl) zirconium screw (p-toluene sulfonate) screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Screw (fluorenyl) zirconium dichloride, ethylene screw (cyclopentadienyl) zirconium dichloride, Ethylene screw (methylcyclopentadienyl) zirconium dichloride, Ethylene screw (dimethylcyclopentadienyl) zirconium dichloride, Ethylene screw (trimethylcyclopentadienyl) zirconium dichloride, Ethylene screw (tetramethylcyclopentadienyl) zirconium dichloride, Ethylene screw (indenyl) zirconium jib ROMIDO ethylene screw (indenyl) zirconium dichloride -- An ethylene screw (indenyl) dimethyl zirconium, an ethylene screw (indenyl) diphenyl zirconium, Ethylene screw (indenyl) methyl zirconium mono-chloride, an ethylene screw (indenyl) zirconium screw (methane sulfonate), An ethylene screw (indenyl) zirconium screw (p-toluene sulfonate), An ethylene screw (indenyl) zirconium screw (trifluoromethane sulfonate), Ethylene screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Isopropylidene (cyclo PENTA diphenyl-fluorenyl) zirconium dichloride, Isopropylidene (cyclopentadienyl-methylcyclopentadienyl) zirconium dichloride, Methylenebis (cyclopentadienyl) zirconium dichloride, methylenebis (methylcyclopentadienyl) zirconium dichloride, Methylenebis (dimethylcyclopentadienyl) zirconium dichloride, Methylenebis (trimethylcyclopentadienyl) zirconium dichloride, Methylenebis (tetramethylcyclopentadienyl) zirconium dichloride, Methylenebis (indenyl) zirconium dichloride, a methylenebis (indenyl) zirconium screw (trifluoromethane sulfonate), Methylenebis (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Methylene (cyclopentadienyl-fluorenyl) zirconium dichloride, Dimethyl silylene screw (cyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (methylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (dimethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (trimethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (tetramethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (indenyl) zirconium dichloride, a dimethyl silylene screw (indenyl) zirconium screw (trifluoromethane sulfonate), Dimethyl silylene screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Dimethyl silylene (cyclo PENTA diphenyl-fluorenyl) zirconium dichloride, Diphenyl silylene screw (indenyl) zirconium dichloride, methylphenyl silylene screw (indenyl) zirconium dichloride, Screw (methylcyclopentadienyl) zirconium dichloride, screw (dimethylcyclopentadienyl) zirconium dichloride, Screw (dimethylcyclopentadienyl) zirconium ethoxy chloride, A screw (dimethylcyclopentadienyl) zirconium screw (trifluoromethane sulfonate), Screw (ethylcyclopentadienyl) zirconium dichloride, screw (methylethyl cyclopentadienyl) zirconium dichloride, A screw (pro PIRUSHI-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dichloride, -1, 2-ethane diyl titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene zirconium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene zirconium dimethyl (the 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) methylene titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene zirconium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene zirconium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dichloride, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dichloride, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium

dibenzyl, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) (Methylamide) -1, 2-ethane diyl titanium dimethyl, dimethyl (methylamide) (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, dimethyl (tetramethyl-eta5-cyclopentadienyl) (methylamide) (tetramethyl - eta 5) - Cyclopentadienyl silane zirconium dichloride, - (tetramethyl (ethyl amide)-eta5-cyclopentadienyl) methylene titanium dichloride, - methylene titanium dimethyl, (Ethyl amide) (tetramethyl-eta5-cyclopentadienyl) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, (The 3rd class butyl amide) Dibenzyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (Benzyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium diphenyl, (Benzyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (2-methoxyphenyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (4-fluoro phenyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) amide titanium dichloride, (2, 6-JI (1-methylethyl) phenyl) (amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (4-methoxyphenyl amide) Dimethyl (1-methylethoxy) silane titanium trichloride, (Tetramethyl-eta5-cyclopentadienyl) 1-(the 3rd class butyl amide)-2-(tetramethyl-eta5-cyclopentadienyl)-1, 1 and 2, 2-tetramethyl disilane titanium dichloride, 1-(the 3rd class butyl amide)-2-(tetramethyl-eta5-cyclopentadienyl)-1, 1 and 2, 2-tetramethyl disilane zirconium dichloride, Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dimethyl, (The 3rd class butyl amide) Dimethyl (eta5-cyclopentadienyl) silane titanium dichloride, (The 3rd class butyl amide) Dimethyl (eta5-cyclopentadienyl) silane zirconium dichloride, (The 3rd class butyl amide) (Anilide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, dimethyl (anilide) (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, etc. are illustrated.

[0041] In this invention, in order to manufacture the polymer which has desired physical properties, the transition-metals compound of the IVB group containing the ligand which has at least two sorts of [A] cyclopentadienyl frames is chosen, and it becomes possible to control the molecular weight of a polymer, a copolymer constituent, etc. by suitable selection to arbitration.

[0042] As a particle (b-1)-like inorganic solid-state of this invention A porosity inorganic solid-state is desirable. For example, SiO₂, aluminum 2O₃, MgO, MgCl₂, ZrO₂, TiO₂, B-2 O₃, CaO, ZnO, The mixture which is BaO, V₂ O₅, Cr 2O₃, ThO, etc., or contains these, Or they are these multiple oxides, for example, SiO₂-MgO, SiO₂-aluminum 2O₃, SiO₂-TiO₂, SiO₂-V₂ O₅, SiO₂-Cr 2O₃, SiO₂-TiO₂-MgO, etc. the inside of these -- SiO₂, aluminum 2O₃, and MgO and MgCl₂ from -- what uses at least one sort of components chosen from the becoming group as a principal component is desirable.

[0043] The particle-like inorganic solid-state of this invention has a hydroxyl group on a front face. In this invention, the hydroxyl group which a particle-like inorganic solid-state has on a front face is usually firmly held under polymerization conditions on a particle-like inorganic solid-state front face, and means the OH radical which generates H₂ O with heating in an elevated temperature.

[0044] The method of obtaining the particle-like inorganic solid-state with which the hydroxyl group was firmly held on the front face under polymerization conditions is based on the approach of leaving a particle-like inorganic solid-state for 3 hours or more, for example under the temperature conditions as the time of a polymerization that it is the same in desiccation nitrogen, or the conditions of the temperature beyond it. The amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face in this invention is expressed by the rate (% of the weight) to the front [heating] particle-like inorganic solid-state weight of the weight decrement of this inorganic solid-state when heating a particle-like inorganic solid-state at 1000 degrees C under ordinary pressure.

[0045] As for the amount of the hydroxyl group which the particle-like inorganic solid-state of this invention has on a front face, it is desirable that it is the amount which commits effectively

an organic (b-2) aluminum oxy compound in case a particle-like inorganic solid-state is supported. In this case, the alkyl group in an organic aluminum oxy compound being crushed with this hydroxyl group, and discovering the catalyst engine performance, if many [too] is checked to the amount of the organic aluminum oxy compound which the amount of this hydroxyl group uses. Moreover, to the organic aluminum oxy compound which the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face uses, if too few, trouble will be caused to support of an organic aluminum oxy compound. When there are too few amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face to an organic aluminum oxy compound, it becomes impossible that is, to support the organic aluminum oxy compound of a desired amount firmly on a particle-like inorganic solid-state front face, although it is thought that the hydroxyl group which a particle-like inorganic solid-state has on a front face reacts with the alkyl group of an organic aluminum oxy compound, and forms O-aluminum association.

[0046] An upper limit is one or less, the range of the mole ratio (OH/Alb -2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which a particle-like inorganic solid-state has on a front face in this invention is 0.7 or less preferably, a minimum is 0.01 or more and it is desirable that it is 0.05 or more preferably.

[0047] Moreover, in order to support the need and an effective quantity of an organic aluminum oxy compound to a polymerization, as for the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face, it is desirable that it is at least 0.5% of the weight or more of a particle-like inorganic solid-state, and it is desirable that it is 1 more % of the weight or more. However, if there are too many amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face, the inclination for activity to fall will be seen. Although it thinks because the reaction site of this with an organic aluminum oxy compound probably increases too much and the effectiveness as a co-catalyst of an organic aluminum oxy compound is restricted as a result, it is unknown for details. Thus, since there is an inclination for activity to fall when there are too many amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face, it is 10 % of the weight more preferably, and the amount of the upper limit of this hydroxyl group is 8 % of the weight still more preferably, and it is it is 12 % of the weight preferably, and desirable [an amount] that it is 6 % of the weight still more preferably.

[0048] In this invention, the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face can be adjusted by heating under suitable conditions if needed. In this invention, the hydroxyl group which a particle-like inorganic solid-state has on a front face can also denaturalize by processing chemically with an organoaluminium compound etc. Thus, when a particle-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face with an organoaluminium compound, it is possible to adjust the amount of this hydroxyl group substantially, and (b-2) the effectiveness of reducing the amount of the organic aluminum oxy compound used is also found out.

[0049] As such an organoaluminium compound, the organoaluminium compound expressed with following general formula **, for example can be illustrated.

$R_5 \text{ n AlX}_{3-n} \dots **$ (R5 is the hydrocarbon group of carbon numbers 1-12 among a formula, X is a halogen or hydrogen, and n is 1-3.) It sets to the above-mentioned general formula **, and is R5. Although it is the hydrocarbon group, for example, the alkyl group, cycloalkyl radical, or aryl group of carbon numbers 1-12 Specifically, they are a methyl group, an ethyl group, n-propyl group, an isopropyl group, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a cyclopentyl group, a cyclohexyl radical, a phenyl group, a tolyl group, etc.

[0050] As such an organoaluminium compound, the following compounds are specifically used. For example, trimethylaluminum, triethylaluminum, triisopropyl aluminum, Alkenyl aluminum, such as trialkylaluminium; isoprenyl aluminum, such as triisobutylaluminum, trioctyl aluminum, and Tori 2-ethylhexyl aluminum; Dimethyl aluminum chloride, a diethylaluminium chloride, Diisopropyl aluminum chloride, diisobutyl aluminum chloride, Dialkyl aluminum halide, such as dimethyl aluminum bromide; Methylaluminium sesquichloride, Ethylaluminium sesquichloride, isopropylaluminium sesquichloride, Alkylaluminium sesquihalide, such as butyl aluminum

sesquichloride and ethylaluminiumsesquibromide; Methyl aluminum dichloride, Ethyl aluminum dichloride, isopropyl aluminum dichloride, ethyl aluminum -- a jib -- alkylaluminum dihalide [, such as ROMIDO,]; -- they are dialkyl aluminum hydrides, such as a diethyl aluminum hydride and a diisobutyl aluminum hydride, etc.

[0051] In this invention, when a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face using the above-mentioned organoaluminium compound, the amount of this organic aluminum used is an amount from which the mole ratio (AIR/OH) to this hydroxyl group (OH) of the aluminum (AIR) in this organic aluminum becomes one or less.

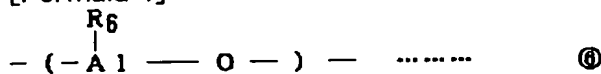
[0052] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face in this invention using the above-mentioned organoaluminium compound, Usually, (b-1) although this hydroxyl group is denaturalized by contacting an organoaluminium compound and a particle (b-1)-like inorganic solid-state before supporting an organic (b-2) aluminum oxy compound into a particle-like inorganic solid-state The denaturation of this hydroxyl group and support of an organic aluminum oxy compound may be performed to coincidence by mixing an organoaluminium compound and an organic (b-2) aluminum oxy compound beforehand, and contacting this mixture and a particle (b-1)-like inorganic solid-state after an appropriate time.

[0053] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face by this invention using the above-mentioned organoaluminium compound, it is considered that the aluminum in the mole ratio (OH/Alb-2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which said particle-like inorganic solid-state has on a front face is the value which added the aluminum (AIR) in this organoaluminium compound. Therefore, the upper limit said whose particle-like inorganic solid-state is the desirable range of the mole ratio (OH/Alb-2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which it has on a front face is one or less, and it is 0.7 or less preferably. The range which a minimum is 0.01 or more and is 0.05 or more preferably When a particle-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face using the above-mentioned organoaluminium compound In order that a particle-like inorganic solid-state may denaturalize the aluminum (Alb-2) and this hydroxyl group in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which it has on a front face An upper limit is one or less, the desirable range of the mole ratio (OH/Alb-2+AIR) to the sum of the aluminum (AIR) in the organic aluminum to be used is 0.7 or less preferably, and a minimum is 0.01 or more and regards or more as 0.05 preferably.

[0054] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face in this invention using the above-mentioned organoaluminium compound, as for the mole ratio (AIR/Alb-2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the aluminum (AIR) in this organoaluminium compound, one or less is desirable. The organic aluminum oxy compound used by this invention (b-2) has the alkyloxy aluminum unit expressed with following type **.

[0055]

[Formula 1]



[0056] (R6 is the carbonization water machine of carbon numbers 1-12 among a formula.) It sets at an above-mentioned ceremony and is R6. A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a decyl group, a cyclohexyl radical, a cyclo octyl radical, etc. can specifically be illustrated. A methyl group and an ethyl group are desirable in these, and especially a methyl group is desirable. In the above-mentioned formula, there are methylalumoxane, ethylalumoxane, n-propyl alumoxane, isopropyl alumoxane, n-buthylalumoxane, isobuthylalumoxane, pentyl alumoxane, hexyl alumoxane, octyl alumoxane, DESHIRU alumoxane, cyclohexyl alumoxane, cyclo octyl alumoxane, etc. as an example of the organic aluminum oxy compound which consists of one kind

of alkylaluminum units. Methylalumoxane and ethylalumoxane are desirable in these and especially methylalumoxane is desirable. Thus, although the organic aluminum oxy compound of this invention is constituted per alkyloxy aluminum expressed with the above-mentioned formula **, it is not necessarily limited to the compound which consists of one kind of configuration unit, and may consist of two or more kinds of configuration units. For example, it is methylethyl alumoxane, methylpropyl alumoxane, methylbutyl alumoxane, etc., and the ratio of various configuration units can be taken to arbitration in 0 - 100% of range. Moreover, you may be the mixture of two or more kinds of organic aluminum oxy compounds which consists of one kind of configuration unit. For example, they are the mixture of methylalumoxane and ethylalumoxane, the mixture of methylalumoxane and n-propyl alumoxane, the mixture of methylalumoxane and isobuthylalumoxane, etc.

[0057] Moreover, the organic aluminum oxy compound of this invention may contain the unreacted chemical which comes from the manufacture approach. That is, generally, although an organic aluminum oxy compound is obtained by the reaction of trialkylaluminum and H_2O , some of these raw materials may remain as an unreacted chemical. For example, in composition of methylalumoxane, trimethylaluminum and H_2O are used as a raw material, but both these both [one of the two or] are the cases where it is contained in methylalumoxane as an unreacted chemical etc. In the manufacture approach of the organic aluminum oxy compound the above-mentioned instantiation, in order to usually use many trialkylaluminums rather than H_2O , trialkylaluminum is contained in an organic aluminum oxy compound as a residual chemical in many cases.

[0058] As a [C] organoaluminum compound (it may be indicated as "component [C] below) used by this invention, the organoaluminum compound expressed with following general formula **, for example can be illustrated.

$R_7 \text{ n AlX}_3\text{-n} \dots$ ** (R_7 is the hydrocarbon group of carbon numbers 1-12 among a formula, X is a halogen or hydrogen, and n is 1-3.) It sets to the above-mentioned general formula **, and is R_7 . Although it is the hydrocarbon group, for example, the alkyl group, cycloalkyl radical, or aryl group of carbon numbers 1-12 Specifically, they are a methyl group, an ethyl group, n-propyl group, an isopropyl group, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a cyclopentyl group, a cyclohexyl radical, a phenyl group, a tolyl group, etc.

[0059] As such an organoaluminum compound, the following compounds are specifically used. Trimethylaluminum, triethylaluminum, triisopropyl aluminum, Alkenyl aluminum, such as trialkylaluminum; isoprenyl aluminum, such as triisobutylaluminum, trioctyl aluminum, and Tri 2-ethylhexyl aluminum; Dimethyl aluminum chloride, a diethylaluminum chloride, Diisopropyl aluminum chloride, diisobutyl aluminum chloride, Dialkyl aluminum halide, such as dimethyl aluminum Promid; Methylaluminum sesquichloride, Ethylaluminum sesquichloride, isopropylaluminum sesquichloride, Alkylaluminum sesquihalide, such as butyl aluminum sesquichloride and ethyl aluminum sesquiPromid; Methyl aluminum dichloride, Ethyl aluminum dichloride, isopropyl aluminum dichloride, ethyl aluminum -- a jib -- alkylaluminum dihalide [, such as ROMIDO,]; -- alkylaluminum hydrides, such as a diethyl aluminum hydride and a diisobutyl aluminum hydride, etc.

[0060] Moreover, as a [C] organoaluminum compound, the compound expressed with following type ** can also be used.

$R_7 \text{ n AlY}_3\text{-n} \dots$ ** (the inside of a formula, and R_7 -- the above -- the same -- Y -OR8 radical --) - OSiR9 3 A radical and -OAlR102 A radical and -NR112 Radical, - SiR123 A radical or -N (R13) AlR142 It is a radical. n is 1-2. R_8 , R_9 , and R_{10} and R_{14} A methyl group, it is an ethyl group, an isopropyl group, an isobutyl radical, a cyclohexyl radical, a phenyl group, etc., R_{11} is hydrogen, a methyl group, an ethyl group, an isopropyl group, a phenyl group, a trimethylsilyl radical, etc., and R_{12} and R_{13} are a methyl group, an ethyl group, etc. Specifically as such an organoaluminum compound, the following compounds are used.

[0061] (i) $R_7 \text{ n aluminum(OR}_8)_3\text{-n}$ The compound expressed, for example, a dimethyl aluminum methoxide, diethyl aluminum ethoxide, diisobutyl aluminum methoxide, etc.

(ii) $R_7 \text{ n aluminum(OSiR}_9)_3\text{-n}$ The compound expressed, for example, Et2aluminum(OSiMe3) (iso-Bu)2 aluminum, (OSiMe3), 2 (iso-Bu) aluminum (OSiEt3), etc.

(iii) R7 n aluminum(OAIR10 <SUB> 2)3-n The compound 2 expressed, for example, Et2 AlOAlEt, and 2 (iso-Bu) AlOAl (iso-Bu)2 etc. .

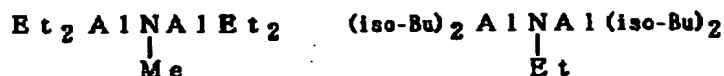
[0062] (iv) -- R7 n aluminum(NR112)3-n Compound 2 expressed, for example, Me2 AlNEt, Et2 AlNHMe, and Me2 AlNHET and Et2 AlN (SiMe3)2 and 2 (iso-Bu) AlN (SiMe3)2 etc. .

(v) -- R7 n aluminum(SiR123)3-n The compound 3 expressed, for example, 2 (iso-Bu) AlSiMe, etc. .

[0063]

[Formula 2]

(vi) $R_7^7 Al (NA_1 R^{14}_2)_3$ で表される化合物、例えば



[0064] In the organoaluminium compound expressed with above-mentioned general formula ** and **, they are R73aluminum and R7n aluminum(OR8)3-n and R7 n3(OAIR102)-n. The organoaluminium compound expressed can be mentioned as a suitable example, and it is R7. It is an isoalkyl group and especially the thing of n= 2 is desirable. Two or more sorts of these organoaluminium compounds can be mixed, and they can also use.

[0065] An IVB group's transition-metals compound with which the catalyst for olefin polymerization concerning this invention contains the ligand which has at least two sorts of [A] cyclopentadienyl frames (it may be indicated as "a component [A]" below), (b-1) Particle-like inorganic solid-state (it may be indicated as "a component (b-1)" below) Organic (b-2) aluminum oxy compound (it may be indicated as "a component (b-2)" below) [B] inorganic solid-state component which it comes to support (it may be indicated as "a component [B]" below) It consists of [C] organoaluminium compounds (it may be indicated as "a component [C]" below) if needed.

[0066] The configuration of the catalyst for olefin polymerization concerning this invention is shown in drawing 1 . As an approach of combining a component [C] two or more sorts of if needed [a component [A], a component [B], and if needed] by this invention For example, [whether a component [C] is respectively introduced directly independently into a polymerization system under polymerization conditions two or more sorts of if needed / a component [A], a component [B], and if needed / and] Or after mixing beforehand two or more sorts of components [A], it is based on the approach of introducing a component [C] directly respectively into a polymerization system under polymerization conditions this component [A] mixture, a component [B], and if needed.

[0067] A component [B] can be adjusted by this invention by mixing a component (b-1) and a component (b-2) in an inert hydrocarbon catalyst. Specifically as this inert hydrocarbon medium, halogenated hydrocarbon or such mixture, such as aromatic hydrocarbon; ethylene chloride, such as alicycle group hydrocarbon; benzene, such as aliphatic hydrocarbon; cyclopentanes, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Deccan, a dodecane, and kerosene, a cyclohexane, and methylcyclopentane, toluene, and a xylene, chlorobenzene, and dichloromethane, etc. can be mentioned.

[0068] It faces mixing a component (b-1) and a component (b-2). A component (b-2) Per 1g (b-1) of components, Usually, it is desirable that it is the range of 10-3 to ten - two mols preferably 5x10-4 to 2xten - two mols, and, as for the concentration of a component (b-2), it is usually desirable for 5x10-2-5 mols /to be [l.] the range of 0.1-3 mols/l. preferably.

[0069] -50-150 degrees C of mixed temperature at the time of mixing a component (b-1) and a component (b-2) are usually -20-120 degrees C preferably. Since it is not necessary to keep it not necessarily constant [the temperature of this mixing] during mixing and the reaction of a component (b-1) and a component (b-2) is rather accompanied by generation of heat (for example, in order to suppress the temperature in early stages of mixing as low as possible and to complete a reaction further), it is desirable to control reaction temperature like making reaction

temperature high at a mixed anaphase. In the case of the above-mentioned example, as desirable temperature in early stages of a reaction, it is -20-30 degrees C preferably, and 50-150-degree C -50-50 degrees C are usually 60-120 degrees C preferably as desirable temperature of a reaction anaphase. Moreover, the contact time of a component (b-1) and a component (b-2) is 1 - 50 hours preferably for 0.5 to 100 hours.

[0070] In this invention, although the activity of a catalyst becomes high and is so advantageous that the atomic ratio (Alb-2 / M) of the aluminum (Alb-2) in a component (b-2) and the transition metals (M) in all components [A] is large in cost, it is one side, and since the price [being general (b-2)] is high, if this atomic ratio is too high, cost will go up on the contrary. Therefore, the range of the atomic ratio (Alb-2 / M) of the aluminum in the component (b-2) of this invention, and the transition metals in all components [A] The upper limit is 2000 preferably and it is 1000 more preferably. It is 500 still more preferably, and is 300 still more preferably, and the minimum is ten or more preferably, it is 20 or more more preferably and it is recommended that they are 30 or more range still more preferably.

[0071] As for the atomic ratio (Alc/Alb -2) of the aluminum atom (Alc) in the component [C] used if needed, and the aluminum atom (Alb-2) in a component (b-2), it is usually desirable 0.01-3, and that it is the range of 0.03-1.5 preferably. As for the catalyst for olefin polymerization of this invention obtained as mentioned above, it is desirable per 1g (b-1) of components to support the aluminum atom of 5×10^{-4} - 5×10^{-2} gram atom preferably about 10-4 to ten to 1 gram atom.

[0072] As an olefin which can carry out a polymerization according to such a catalyst for olefin polymerization The alpha olefin of 3-20, for example, a propylene, ethylene and a carbon number 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, cyclopentene, a cyclo heptene, Norbornene, 5-methyl-2-norbornene, tetracyclo dodecen, the 2-methyls 1, 4, and 5, 8-dimethano - 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene etc. can be mentioned. Furthermore, styrene, a vinyl cyclohexane, and dienes can also be used.

[0073] this invention -- a polymerization -- a suspension-polymerization method or a vapor-phase-polymerization method -- it can carry out also in any. The same thing as the inert hydrocarbon solvent used in the suspension-polymerization method on the occasion of component [B] adjustment can be used, and the olefin itself can also be used as a solvent. The range of -50-150 degrees C of polymerization temperature of the olefin using such a catalyst for olefin polymerization is usually 0-100 degrees C preferably. the polymerization preasure force - - usually -- ordinary pressure -100 kg/cm2 -- desirable -- ordinary pressure -50 kg/cm2 It is under a condition and a polymerization reaction can be performed also in which approach of a batch process, half-continuous system, and continuous system.

[0074] The polymerization of this invention is performed using a multistage polymerization method. That is, a polymerization is performed by performing a polymerization gradually by letting it pass one by one to the curing units which arranged curing units in the serial and arranged the polymerization product in the middle of a catalyst component or/and a polymerization in this serial. In this invention, it can adjust depending on how of selection of a suitable component [A], the class of at least two sorts of components [A], and an amount to combine, and also the molecular weight of an olefin polymer can be adjusted by making hydrogen exist in a polymerization system, or changing polymerization temperature. In addition, in this invention, the catalyst for olefin polymerization can contain other useful components in olefin polymerization besides each above component.

[0075]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these examples. In addition, in this invention, the physical properties of an ethylene system polymer are the following, and are made and measured.

[Consistency] The consistency in this invention was measured according to ASTM-D -1505.

[0076] [MI and HMI] MI and HMI in this invention are ASTM respectively. It is measured according to the conditions E in D1238, and Conditions F.

[Melting tension] It can ask for the melting tension (MT) in this invention by measuring the stress when extending the polymer which carried out melting with constant speed. In this

invention, melting tension was measured using the Oriental energy machine factory melt tension measurement machine on conditions with a part for /, a resin temperature [of 190 degrees C], and part [for /] and diameter of 10-20mm nozzle in extrusion rate winding rate of 10mm 2.09mmphi, and a nozzle die length of 8mm. in addition -- the time of melting tension measurement -- a polymer -- beforehand -- as a thermostabilizer -- a 2 and 6-Jl t butyl PARAKU resol -- 0.1wt(s)% -- it adds.

[0077] [Izod impact value] The Izod impact value in this invention is JIS. K The value for which 7110 can be asked according to the approach of a publication is said.

[ESCR] The environmental-stress-cracking-proof value (ESCR) in this invention is JIS. K According to 6760, it asks as 50% crack generating time amount in the approach of a constant strain environmental-stress-cracking trial.

[Dirt impact resistance value] A film with a thickness of 30 micrometers which formed membranes on the same membrane formation conditions is used for the dirt impact resistance value of this invention, and it is JIS. K 7124 was asked according to the approach of a publication.

[2% modulus] A film with a thickness of 30 micrometers which formed membranes on the same membrane formation conditions is used for 2% modulus in this invention, and it is JIS. K It asked by measuring a modulus value when distortion of a film reaches to 2% according to 7127.

[0078] (Example 1)

[Adjustment of a methylalumoxane support silica] Silica (pore volume of 1.10cm³ / g, and specific surface area are 318cm² / g, bulk density 0.38 g/cm³, and amount of surface water acid radicals 4.1wt%) 4.0g and toluene 40ml were put into 200ml glass flask which fully carried out the nitrogen purge, and it was made the letter of suspension, and cooled to -5 degrees C. Into this suspension, 30ml (Tosoh Akzo MMAO-3A, aluminum;1.15mol/l) of toluene solutions of methylalumoxane was dropped in 1 hour, keeping the temperature of suspension at -5 degrees C. Then, it performed at 0 degree C, the reaction was further performed under reflux conditions at the room temperature for 3 hours for 1 hour for 1 hour, it cooled to 20 degrees C after reaction termination, and the suspension of the silica which supported methylalumoxane was obtained.

[0079] [Polymerization] 0.80l. of hexanes was put into the autoclave made from stainless steel of 1.6l. of content volume which fully carried out the nitrogen purge, and 0.35 mols of 1-hexenes were added. After adding 0.5 millimols of silica suspension adjusted to this like the above by aluminum conversion, 15Nml addition of the hydrogen was carried out, ethylene was introduced further, 7kg/cm² of total pressure was set to -G, and temperature in a system was made into 60 degrees C. 0.5 micromole of toluene solutions of screw (n-butylcyclopentadienyl) zirconium dichloride was added by zirconium conversion after that, temperature in a system was made into 70 degrees C, and the 1st step of polymerization was started. Then, the polymerization of eye this one stage was continued at 70 degrees C, having supplied ethylene and maintaining 7kg/cm² of total pressure at -G.

[0080] After [of the 1st step of polymerization initiation] 40 minutes, in order to perform the 2nd step of polymerization, after once purging the hydrogen in a polymerization system and newly adding the toluene solution of screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride into a 0.5 micromole polymerization system by zirconium conversion, the 2nd step of polymerization was started, having supplied ethylene again and having used 7kg/cm² of total pressure as -G. In this example, after newly adding screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride in a polymerization system, it considered as the 2nd step of polymerization. Then, after performing a polymerization for 20 minutes, the 2nd step of polymerization was ended. After it filtered the polymer after the 2nd step of polymerization termination and the methanol washed, one evening dried at 50 degrees C. In addition, adhesion of a polymer etc. was not accepted in the wall surface of a polymerization reactor. The operation conditions and polymerization result of this example 1 were shown in Table 1 and 2, respectively.

[0081] (Examples 2-6) the class of metallocene in each polymerization stage and its number of use classes, a comonomer, and the amount of hydrogenation -- polymerization time amount etc.

was changed further, and also the polymerization of each stage was carried out like the example 7. The operation conditions and polymerization result of each example were shown in Table 1 and 2.

[0082] (Example 7)

[Adjustment of a methylalumoxane support silica] The suspension of the silica which carried out like the example 1 and supported methylalumoxane was obtained.

[Polymerization] After putting 0.80l. of hexanes into the autoclave made from stainless steel of 1.6l. of content volume which fully carried out the nitrogen purge, 0.5 millimols of silica suspension adjusted like the above were added by aluminum conversion. 15ml of hydrogen was added to this, ethylene was introduced further, 7kg/cm² of total pressure was set to -G, and temperature in a system was made into 60 degrees C. 0.5 micromole of toluene solutions of screw (n-butylcyclopentadienyl) zirconium dichloride was added by zirconium conversion after that, temperature in a system was immediately made into 70 degrees C, and the 1st step of polymerization was started.

[0083] The polymerization of eye this one stage was continued having supplied ethylene after that and maintaining 7kg/cm² of total pressure at -G. in order to perform the 2nd step of polymerization after [of polymerization initiation] 20 minutes -- the hydrogen in a polymerization system -- once -- purging -- new -- the toluene solution of screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride -- zirconium conversion -- 0.5 micromole -- adding -- further -- after adding 0.10 mols of 1-hexenes, the 2nd step of polymerization was started, having supplied ethylene again and having used 7kg/cm² of total pressure as -G. Then, after performing a polymerization for 40 minutes, having supplied ethylene and maintaining 7kg/cm² of total pressure at -G, the polymerization of eye these two stages was ended.

[0084] After it filtered the polymer after polymerization termination and the methanol washed, one evening dried at 50 degrees C. In addition, adhesion of a polymer etc. was not accepted in the wall surface of a polymerization reactor. The operation conditions and polymerization result of this example 2 were shown in Table 1 and 3, respectively.

[0085] (Examples 8-10) the class of metallocene in each polymerization stage and its number of use classes, a comonomer, and the amount of hydrogenation -- polymerization time amount etc. was changed further, and also the polymerization of each stage was carried out like the example 7. The operation conditions and polymerization result of each example were shown in Table 1 and 2.

[0086] (Example 1 of a comparison) In the polymerization of an example 1, except having carried out the 1st step of polymerization for 60 minutes, having used the addition of 0.35 mols and hydrogen as 15ml for the addition of 1-hexene, and having not carried out the 2nd more step of polymerization, a polymerization, after treatment, etc. were carried out in the same procedure as an example 1, and the polymer was obtained. These operation conditions and a polymerization result were shown in Table 1 and 2, respectively.

[0087] (Example 2 of a comparison) In the polymerization of an example 7, except having added 0.05 mols of 1-hexenes, having carried out the 1st step of polymerization for 60 minutes, and having not carried out the 2nd more step of polymerization, a polymerization, after treatment, etc. were carried out in the same procedure as an example 7, and the polymer was obtained. The operation condition and a polymerization result were shown in Table 1 and 3, respectively.

[0088]

[Table 1]

	MAO (μmol)	1 段 目				2 段 目				
		Zr 1 (μmol)	1-ヘキセン (mol)	H ₂ (ml)	重合時間 (min)	Zr 2 (μmol)	Zr 3 (μmol)	1-ヘキセン (mol)	H ₂ (ml)	重合時間 (min)
実施例 1	0.5	A, 0.5	0.35	15	40	D, 0.5	---	—	—	20
実施例 2	0.5	A, 0.5	0.35	10	40	D, 0.5	---	—	—	20
実施例 3	0.5	D, 0.5	0	0	10	B, 0.5	---	0.35	3	50
実施例 4	0.5	E, 0.5	0	0	10	B, 0.5	---	0.35	3	50
実施例 5	0.5	E, 0.5	0	0	15	A, 0.25	B, 0.25	0.35	10	45
実施例 6	0.5	E, 0.5	0	0	15	A, 0.25	B, 0.25	0.15	10	45
比較例 1	0.5	A, 0.5	0.30	10	60	---	---	—	—	—
実施例 7	0.5	A, 0.5	0	15	20	D, 0.5	---	0.35	—	40
実施例 8	0.5	E, 0.5	0	0	15	A, 0.5	B, 0.5	0.05	15	45
実施例 9	0.5	B, 0.25	0	40	30	A, 0.75	---	0.05	0	30
実施例 10	0.5	B, 0.5	0.05	0	10	D, 0.5	---	0.0	10	50
比較例 2	0.5	A, 0.5	0.05	15	60	---	---	—	—	—

(注) A: ビス (n-ブチルシクロペンタジエニル) ジルコニウムジクロリド

B: エチレンビス (インデニル) ジルコニウムジクロリド

C: ビス (1, 3-ジメチルシクロペンタジエニル) ジルコニウムジクロリド

D: ビス (1, 2, 3, 4, 5-ペンタメチルシクロペンタジエニル) ジルコニウムジクロリド

E: ヒドロトリシラゾリルボレート (シクロペンタジエニル) ジルコニウムジクロリド

[0089]

[Table 2]

	MI (g/10min)	HMI (g/10min)	MIR	d (g/cm ³)	MT (g)	DIS (g)	2%モジュラス (kgf/cm ²)
実施例 1	1.5	52.7	35.1	0.921	7.1	1300	3100
実施例 2	1.1	33.6	30.5	0.915	8.5	1400	2000
実施例 3	1.0	32.0	32.0	0.908	9.1	1800	1550
実施例 4	0.92	28.7	31.2	0.902	8.7	>2000	1300
実施例 5	3.2	122.6	38.3	0.910	5.5	1580	1700
実施例 6	2.5	96.5	38.6	0.935	6.3	450	5700
比較例 1	1.5	0.14	15.1	0.924	2.2	600	2000

[0090]

[Table 3]

	MI (g/10min)	HMI (g/10min)	MIR	d (g/cm ³)	MT (g)	I z o d (kgf/cm/cm ²)	ESCR (hr)
実施例 7	0.44	16.5	37.5	0.953	24.5	35	> 1000
実施例 8	0.57	20.9	36.6	0.956	20.0	25	800
実施例 9	5.8	263	45.4	0.965	7.5	45	> 1000
実施例 10	0.35	13.4	38.3	0.959	27.8	41	> 1000
比較例 2	0.54	10.6	19.7	0.956	2.5		300

[0091]

[Effect of the Invention] The catalyst which consists of an organic aluminum component if needed [the inorganic solid-state component and if needed] which supported the transition-metals compound and the organic aluminum oxy compound is used. By combining a multistage

polymerization method and the polymerization method using at least two sorts of transition-metals compounds It becomes controllable [the molecular structure of a polymer, a microstructure macrostructure, etc.] by each structure level, and a synergistic effect is discovered by optimizing structure in each structure level, and the olefin system polymer which has the surprising engine performance which was not able to be obtained at all is obtained with the conventional technique.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacture approach of the olefin system polymer which has the outstanding physical properties, and its polymer. In more detail The approach and multistage polymerization method using the catalyst which consists of an inorganic solid-state component which supported the transition-metals compound and the organic aluminum oxy compound, and the polymerization method using at least two sorts of transition-metals compounds Combination, It is related with the polymer obtained by this manufacture approach about the approach of manufacturing the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, by performing structure control on each structure level, such as the molecular structure of a polymer, a microstructure, and macrostructure.

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PRIOR ART

[Description of the Prior Art] As a catalyst for manufacturing the polymer of an olefin from the former, the so-called Ziegler Natta catalyst which consists of a titanium compound and an organoaluminium compound is known. By using the catalyst which consists ethylene or ethylene, and other 1-olefins of alumoxane which is one sort of the halogen content transition-metals compound of fusibility, such as screw (cyclopentadienyl) zirconium dichloride, and an organic aluminum oxy compound in polymerization activity high on the other hand in recent years, the technique which carries out a polymerization in high activity was found out, and it became well-known at JP,58-19309,A.

[0003] as the usage of a catalyst system which furthermore consist of the above-mentioned transition metals compound and an organic aluminum oxy compound, it be base on the approach depending on control of the conventional hydrogen concentration or polymerization temperature, but the method of adjust the molecular weight and the comonomer content of an olefin system polymer be also propose by JP,60-35007,A by the approach of choose the transition metals compound according to the purpose from the transition metals compounds of the varieties containing the above-mentioned transition metals compound.

[0004] Since a polymerization is possible, the polymer with narrow molecular weight distribution is further excelled also in copolymeric and the catalyst system which consists of this transition-metals compound and an organic aluminum oxy compound can obtain a polymer with many comonomer contents, and the uniform polymer of comonomer distribution compared with the so-called Ziegler Natta catalyst, it has the description that the polymer which has the physical properties which were excellent in shock resistance, solvent resistance, etc. can be obtained.

[0005] However, the advance of the latest industry is remarkable, and by the time a rise of the expectation for the polyolefine from the standpoint of an environmental problem fully fills this military requirement only with the military requirement to polyolefine only using conjointly extensive and the catalyst system which has a high level and consists of the above-mentioned transition-metals compound and an organic aluminum oxy compound by leaps and bounds, it will not result, but much more improvement in the engine performance is called for strongly.

[0006] Furthermore, since this catalyst system was meltable to a solvent, when applying to a suspension-polymerization method or a vapor-phase-polymerization method, the description of the polymer obtained was very bad, and adhered to a wall surface, an impeller, etc. of a reactor, and it had the problem that it could not be used the way things stand industrially. Moreover, that the molecular weight distribution of a polymer are narrow also had the practical big problem of causing the fall of fabrication nature by one side, although it was advantageous in order to acquire the physical properties which were excellent like the above. The present condition is that the catalyst system which consists of a transition-metals compound and an organic aluminum oxy compound has not resulted in the full-scale industrialization by the suspension-polymerization method and the vapor-phase-polymerization method in addition now because of these problems.

[0007] Therefore, development of the polymerization method using the catalyst system containing the transition-metals compound performed so far and an organic aluminum oxy compound put [rather than] weight on the above-mentioned problem solvings, such as an

improvement of the shape of polymerization somatic, and an improvement of fabrication nature, rather aiming at much more improvement in polymer physical properties. For example, in order that the description of a polymer may solve the problem of being very bad, the attempt which porous inorganic oxides, such as a silica, an alumina, and a silica alumina, are made to support one [at least] component of a transition-metals compound and an organic aluminum oxy compound, and uses it for olefin polymerization is made.

[0008] Moreover, the approach using the multistage polymerization method which is a well-known technique as an approach of improving fabrication nature is proposed. For example, in JP,3-234717,A, the method of improving the melting property of a polymer is indicated by the multistage polymerization method using the catalyst for olefin polymerization which consists of the above-mentioned transition-metals compound and an organic aluminum oxy compound. Moreover, the approach of mixing and using at least two sorts of transition-metals compounds as other means to improve fabrication nature, and making molecular weight distribution large is proposed by JP,60-35008,A. It is also collectively indicated by JP,60-35008,A that a transition-metals compound can be supported to porous inorganic support, such as a silica, an alumina, and a silica alumina.

[0009] Furthermore, for JP,5-155932,A and JP,5-155933,A, the particle-like support which has at least two or more sorts of transition-metals compounds, the amount of water of adsorption of the specific range, and the amount of a surface water acid radical is used, precuring is performed to them, and the method of improving physical properties, such as the shape of the melting tension of an olefin system polymer and corpuscular character, and improving fabrication nature is indicated.

[0010] Each these conventional approach aimed at improvement in fabrication nature, and was far from a viewpoint of much more improvement in polymer physical properties. Moreover, about the improvement of fabrication nature itself, although the conventional approach showed a certain amount of improvement effect, it was not necessarily able to be said to be enough. for example, by the multistage polymerization method, acquiring desired molecular weight distribution only by control of polymerization conditions has constraint, and by the approach using at least two sorts of transition-metals compounds It is difficult to find out the combination of a transition-metals compound suitable in order to acquire desired molecular weight distribution as a matter of fact. It is general to need costs and an effort great by it, even if it is able to find out the combination of such a transition-metals compound. The transition-metals compound moreover found out was a special compound, and also when very expensive, there was a not few problem and it was not practical.

[0011] On the other hand, the manufacturing method of the reaction blend using at least two sorts of transition-metals compounds is proposed in JP,5-310831,A. The approach using two or more reactors is also illustrated by JP,5-310831,A as a mixed means.

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EFFECT OF THE INVENTION

[Effect of the Invention] The catalyst which consists of an organic aluminum component if needed [the inorganic solid-state component and if needed] which supported the transition-metals compound and the organic aluminum oxy compound is used. By combining a multistage polymerization method and the polymerization method using at least two sorts of transition-metals compounds It becomes controllable [the molecular structure of a polymer, a microstructure macrostructure, etc.] by each structure level, and a synergistic effect is discovered by optimizing structure in each structure level, and the olefin system polymer which has the surprising engine performance which was not able to be obtained at all is obtained with the conventional technique.

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JP,08-053509,A [TECHNICAL PROBLEM]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, it is premised on using the catalyst which all supported the transition-metals compound in the conventional approach when applying to a suspension-polymerization method or a vapor-phase-polymerization method. When performing a multistage polymerization based on this approach, even if it newly adds the transition-metals compound supported with the latter polymerization Since the polymer by which a polymerization is carried out with the transition-metals compound added in the latter part, and the polymer by which a polymerization is carried out with the transition-metals compound which came from the preceding paragraph turn into a polymer of ***** another kind which are [distribution / molecular weight, / presentation] different according to each catalyst, In order for the polymer of these another kind to generate independently for every support with which each catalyst was supported, therefore to grow up to be the particle of the polymer of these another kind, respectively, It became the same thing as having mixed the particles of the polymer of these another kind as a matter of fact, therefore there was a problem [polymers] that it was difficult the uniform sea island structure for every presentation unit and to go back to the microstructure in crystal level further, and to mix to homogeneity as a matter of fact.

[0013] For this reason, in case a multistage polymerization is performed, even if it adds a new transition-metals compound at a latter polymerization process based on the conventional technique and performs a polymerization The same thing as the mixture of mere polymer powder is obtained. In being severe in not accepting a practical merit in the physical properties of a polymer at all an uneven presentation distribution of the obtained polymer sake -- the fall of a mechanical strength, generating of gel, etc. -- good -- since it was better, colander evil was also generated, and practical use was not able to be presented.

[0014] And if a multistage polymerization method and the approach using at least two sorts of transition-metals compounds are applied For example, the structure control with molecular levels, such as a molecular weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, Control of microstructures, such as a distributed condition in crystal size, crystallinity, and crystal level, Furthermore, things for which each structure is controlled the optimal in each structure level of a polymer, such as control of macrostructures, such as sea island structure for every presentation unit, become possible. There were a purport which can manufacture the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, and no example indicated concretely. Rather than it applies the describing [above] multistage polymerization method and the approach using at least two sorts of transition-metals compounds furthermore, as a concrete example For example, although it becomes possible to control molecular weight distribution in the easy and broad range by adopting the polymerization conditions on which a different new transition-metals compound from the transition-metals compound used for the polymerization of the preceding paragraph is added, and polymerization conditions also differ from the polymerization conditions of the preceding paragraph in case a latter polymerization is performed The indication of such an example was not seen at all conventionally.

[0015] This invention offers the polymer obtained by the manufacture approach of the olefin system polymer substantially mixed with homogeneity, and its approach. Furthermore, molecular

weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, Distribution of the structure control with molecular levels, such as the mixed state of molecules, crystal size, and this crystal size, Further control of macrostructures, such as sea island structure for every presentation unit, etc. control of microstructures, such as a distributed condition in crystallinity and crystal level, and by controlling each structure the optimal in each structure level of a polymer It aims at offering the polymer obtained by the method of manufacturing the olefin system polymer which has the physical properties which were excellent by leaps and bounds compared with the former, and its approach.

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MEANS

[Means for Solving the Problem] In the catalyst system which this invention persons become from a transition-metals compound and an organic aluminum oxy compound The result of having repeated research wholeheartedly in order to aim at improvement in physical properties of the polymer obtained, If the approach and multistage polymerization method using the catalyst which consists of an organic aluminum component if needed [the inorganic solid-state component and if needed] which supported the transition-metals compound and the organic aluminum oxy compound, and the polymerization method using at least two sorts of transition-metals compounds are combined Control on each structures level, such as the molecular structure of a polymer, a microstructure, and macrostructure, is possible. By optimizing structure in each structure level, a synergistic effect is discovered and it came to make a header and this invention for the olefin system polymer which has the surprising engine performance which was not able to be obtained at all being obtained with the conventional technique.

[0017] This invention At least two sorts of [A] cyclopentadienyl frames The catalyst for olefin polymerization which will serve as a transition-metals compound of the IVB group containing the ligand which it has, and an inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle-like inorganic solid-state which has a hydroxyl group on the [B] (b-1) front face from the [C] organoaluminium compound if required is used. Furthermore, it sets in at least one polymerization stage among the polymerization stages after the 2nd step using a multistage polymerization in the case of this multistage polymerization. By newly adding the transition-metals compound of the IVB group containing the ligand which has at least one sort of different cyclopentadienyl frames from the transition-metals compound of the IVB group containing the ligand which has the cyclopentadienyl frame added to the 1st step, and performing a polymerization, the molecular structure of a polymer, The approach of manufacturing the olefin system polymer which controls each structures level, such as a microstructure and macrostructure, and has the outstanding physical properties is offered, and the polymer obtained by this manufacture approach is offered.

[0018] Hereafter, the olefin system polymer by which a polymerization is carried out by the multistage polymerization method and this approach of the olefin concerning this invention is indicated concretely. In addition, in this invention, it may be used with a "polymerization" in the semantics which included not only homopolymerization but copolymerization, and may be used with a "polymer" in the semantics which included not only a homopolymer but the copolymer.

[0019] When olefin polymerization is performed by this invention using the catalyst for olefin polymerization which will serve as [A] transition-metals compound and [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle (b-1)-like inorganic solid-state from the [C] organoaluminium compound if required, [A] In order that a transition-metals compound and the organic (b-2) aluminum oxy compound supported on [B] inorganic solid-state component may form the polymerization active spot, A polymer is generated on [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported, and [B] inorganic solid-state component grows up to be a polymer particle as a result. If two or more sorts of [A] transition-metals compounds exist in a polymerization system in the case of a polymerization, two kinds of polymers will generate

according to [** A] transition-metals compound. In this case, in order to generate the polymer of these two classes on the same [B] inorganic solid-state component at coincidence, the polymer particle to which two kinds of polymers were substantially mixed with homogeneity with the molecular level as a result is obtained. Thus, it became possible to manufacture the polymer, considered that it cannot be at all conventionally as a result of mixing two kinds of polymers with homogeneity with a molecular level substantially. For example, mixing with the ethylene polymer of the amount of giant molecules and the ethylene polymer of low molecular weight was not mixed with homogeneity if the ethylene polymer which has the molecular weight of the interstitial segment of this amount part of giant molecules and a low-molecular-weight part did not exist, but it caused the fall of a mechanical strength, and generating of gel, and has been considered that it cannot mix and use it at all. However, it became possible to mix the amount ethylene polymer of giant molecules, and a low-molecular-weight ethylene polymer with a direct molecular level, without making the ethylene polymer which has the molecular weight of this interstitial segment exist, when using the approach of this invention.

[0020] It depends on coordination force, polymerization activity, etc. over the organic aluminum oxy compound of a transition-metals compound for the mixed ratio of two kinds of polymers which are this invention, for example, are generated when making two sorts of transition-metals compounds live together in one polymerization stage and carrying out the polymerization of the mixture of a polymer. By following, for example, choosing a suitable transition-metals compound in the example of mixing of the above-mentioned amount ethylene polymer of giant molecules, and a low-molecular-weight ethylene polymer, it is possible to control the quantitative ratio of the amount part of giant molecules of an ethylene polymer and a low-molecular-weight part, therefore if this technique is used, a polymerization is possible for the ethylene polymer which has a desired molecular weight distribution. Thus, it is possible to control a polymer by this invention with a molecular level.

[0021] The polymerization of the polymer with which two kinds of polymers were substantially mixed with the surprising thing with the molecular level is realizable even if it adds gradually two sorts of [A] transition-metals compounds. For example, when using one sort of transition-metals compounds first, performing a polymerization, adding the transition-metals compound of another kind after that and performing a polymerization, in the first polymerization, the polymer according to the transition-metals compound used first generates, and the polymer with which two kinds of polymers according to the transition-metals compound and the transition-metals compound of this another kind which were used for the beginning from the time of adding the transition-metals compound of another kind after that were mixed with homogeneity generates. The polymer obtained turns into a polymer which the polymer obtained first and the polymer with which two kinds of polymers were mixed with homogeneity were mixed, and became sea island structure as a result of such a polymerization. If the quantitative ratio of the polymer obtained first and the polymer with which two kinds of polymers were mixed with homogeneity is controlled, it will become possible to control the sea island structure of the polymer finally obtained.

[0022] Like this example, by newly adding the transition-metals compound of another kind after the first polymerization, it was what is not expected that the polymerization based on an another kind transition-metals compound arises, and it was a just surprising thing from the common sense of the conventional technique. Namely, the thing usually predicted in the example like the above From what will be covered with the polymer which the polymerization active spot formed on support generated by the first polymerization Even if it newly adds the transition-metals compound of another kind after that, the transition-metals compound of this another kind cannot contact the organic aluminum oxy compound on support. Therefore, the polymerization activity with the transition-metals compound of this another kind that could not form the polymerization active spot but was newly added is being unable to expect.

[0023] However, even if it newly adds the transition-metals compound of another kind after the first polymerization like the above-mentioned example in the catalyst system of this invention to a surprising thing, the polymerization activity based on the transition-metals compound of this another kind is discovered. Although it is thought that this has suggested the transition-metals

compound of this another kind reaching to the organic aluminum oxy compound which diffused the inside of the polymer made first and was supported by the inorganic solid-state component, and forming the polymerization active spot, it is unknown for details.

[0024] By this invention, in order to expand the effectiveness of this polymerization further, a polymerization is performed by the multistage polymerization. That is, when newly adding the transition-metals compound of another kind, the polymerization conditions which differ from the first polymerization conditions by the multistage polymerization are adopted, and much more optimization of polymer structure is enabled. The multistage polymerization method as used in the field of this invention means the polymerization method which performs a polymerization gradually by letting it pass one by one to the curing units which arranged curing units in the serial and arranged the polymerization product in the middle of a catalyst component or/and a polymerization in this serial.

[0025] The catalyst for olefin polymerization which will serve as [A] transition-metals compound and [B] inorganic solid-state component with which the organic (b-2) aluminum oxy compound was supported by the particle (b-1)-like inorganic solid-state from the [C] organoaluminium compound in the multistage polymerization of this invention if required is used. In at least one polymerization stage, at least one sort of different transition-metals compounds from the transition-metals compound added to the 1st step are newly added among the polymerization stages after the 2nd step, and a polymerization is performed. Therefore, in this invention, at least two sorts of [A] transition-metals compounds are used. Moreover, in the multistage polymerization of this invention, a polymerization monomer besides a catalyst component, a comonomer, a solvent, etc. may be added in the polymerization stage after the 2nd step. By controlling the classes and amounts of an additive other than such a catalyst component, the width of structure control of a polymer can be extended further.

[0026] For example, at the time of the 1st step of polymerization, use the transition-metals compound which ethylene can giant-molecule quantify, perform the gay polymerization of ethylene, and the polymerization of the ultrahigh-molecular-weight ethylene polymer is carried out. If an alpha olefin is added as the transition-metals compound which was newly excellent in copolymeric with the 2nd step of polymerization, and a comonomer component and a low consistency ethylene polymer is made into a polymerization It is possible to manufacture the polymer in which the ultrahigh-molecular-weight ethylene polymer carried out micro-disperse to the polymer or low consistency ethylene polymer which was not in the former, and in which the low consistency ethylene polymer carried out micro-disperse to the ultrahigh-molecular-weight ethylene polymer. By controlling such sea island structure suitably, extrusion molding and injection molding of an ultrahigh-molecular-weight ethylene polymer impossible former absolutely become possible.

[0027] In this invention, processes which do not perform a polymerization substantially, such as a mixed process, a degasifying process, cooling, or a temperature up process, may be between the curing units located in a line with the serial. Structure control of a polymer will not be attained without the polymerization method using the catalyst system of this invention, and this. Therefore, according to the approach of this invention, manufacture of synergy polyolefine is attained.

[0028] The synergy polyolefine as used in the field of this invention means further the olefin system polymer whose physical properties improved by leaps and bounds compared with the polyolefine by the conventional technique control of microstructures, such as molecular structure control, crystal sizes and degree of crystallinity, such as molecular weight distribution, comonomer distribution in a chain, and comonomer distribution between molecules, and an array of a crystal, and by [, such as control of macrostructures, such as sea island structure for every presentation unit,] controlling each structure the optimal in each structure level of a polymer. In the combination of the physical properties that whose it was the physical properties which conflict with the conventional technique, and was made compatible in such an olefin system polymer it was made impossible, it is also possible to raise both physical properties.

[0029] Thus, it is thought that it is based on the synergistic effect by optimization on each structures level, such as the above-mentioned molecular structure, a microstructure, and

macrostructure, that the physical properties which were excellent by leaps and bounds are realizable, and optimization on such each structure level becomes realizable for the first time by the approach of this invention. The improvement in fast of the physical properties in this invention means the case where 30% or more of improvement is made for example, in view physical properties etc.

[0030] As a concrete example of the above-mentioned synergy polyolefine, although the ultra high molecular weight polyethylene in which said extrusion molding and injection molding are possible is mentioned, for example, the polyethylene which has realized having the high rigidity and high shock resistance which have been considered not to coexist conventionally, and high ESCR is mentioned as other examples by carrying out micro-disperse of the low density polyethylene with uniform comonomer distribution with a narrow ($M_w/M_n=2-5$) molecular weight distribution into high density polyethylene.

[0031] As still more nearly another example, extrusion-molding nature and a die swell are improved by controlling molecular weight distribution the optimal, ESCR and shock resistance are raised by controlling the comonomer content in each molecular weight the optimal further, and the polyethylene which has realized having a moldability, high ESCR, and high shock resistance as the result is mentioned.

[0032] According to the approach of this invention, it is possible to manufacture the polyolefine which has the outstanding engine performance which was not able to be obtained at all with the conventional technique in this way. In especially an ethylene system polymer, the effectiveness is greatest. This invention is explained still more concretely below. As a transition-metals compound of the IVB group containing the ligand which has [A] cyclopentadienyl frame used by this invention, the compound expressed with following general formula ** can be illustrated. $ML_x \dots$ ** [0033] the above-mentioned general formula ** -- setting -- M -- the [periodic table], although it is an IVB group's transition metals It is a zirconium, titanium, or a hafnium and L is specifically a ligand configured in transition metals. At least one L A carbon number L other than the ligand which is a ligand which has a cyclopentadienyl frame and has a cyclopentadienyl frame The hydrocarbon group of 1-12, An alkoxy group, an aryloxy radical, a halogen atom, a trialkylsilyl group, $-SO_3 R$ (however, R is the hydrocarbon group of the carbon numbers 1-8 which may have substituents, such as a halogen.) Or it may be a hydrogen atom, or you may be a hetero 3 seat ligand, and x is the valence of transition metals.

[0034] As a ligand which has a cyclopentadienyl frame For example, a cyclopentadienyl group or a methylcyclopentadienyl radical, A dimethylcyclopentadienyl radical, a trimethylcyclopentadienyl radical, A tetramethylcyclopentadienyl radical, a pentamethylcyclopentadienyl group, An ethylcyclopentadienyl radical, a methylethyl cyclopentadienyl group, A propylcyclopentadienyl radical, a methylpropyl cyclopentadienyl group, Alkylation cyclopentadienyl groups, such as a butylcyclopentadienyl radical, a methylbutyl cyclopentadienyl group, and a hexyl cyclopentadienyl group, or an indenyl group, 4, 5 and 6, a 7-tetrahydro indenyl group, a fluorenyl group, etc. can be illustrated. The halogen atom, the trialkylsilyl group, etc. may permute these radicals, and the hetero atom which can serve as a joint seat further may permute them. Moreover, the cyclopentadienyl frame of this invention may contain the hetero atom in the frame.

[0035] Especially in the ligand configured in these transition metals, an alkylation cyclopentadienyl group is desirable. When the compound expressed with the above-mentioned general formula ** contains two or more ligands which have a cyclopentadienyl frame, the ligand which has two cyclopentadienyl frames among those may be combined through permutation silylene radicals, such as permutation alkylene group; silylene radicals, such as alkylene group; isopropylidene, such as methylene, ethylene, and a propylene, and diphenylmethylene, or a dimethyl silylene radical, a diphenyl silylene radical, and a methylphenyl silylene radical, etc.

[0036] By this invention, the following is mentioned as a more concrete example of ligands other than the ligand which has a cyclopentadienyl frame. For example, specifically, aralkyl radicals, such as aryl groups, such as cycloalkyl radical; phenyl groups, such as alkyl group; cyclopentyl groups, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, and a decyl group, a cyclohexyl radical, and a cyclo octyl radical, and a tolyl group, benzyl, and a neo fill radical, are illustrated for

a carbon number as a hydrocarbon group of 1-12.

[0037] Moreover, as an alkoxy group, a methoxy group, an ethoxy radical, a butoxy radical, etc. are illustrated. A phenoxy group etc. is illustrated as an aryloxy radical. Moreover, a fluorine, chlorine, a bromine, iodine, etc. are illustrated as a halogen atom. As a ligand furthermore expressed with $-SO_3 R$, a p-toluene sulfonate group, a methane sulfonate group, a trifluoromethane sulfonate group, etc. are illustrated. Furthermore as a hetero 3 seat ligand, a hydronalium tris pyrazolyl borate radical, a TORISUBISU phenyl oxo-phosphoranyl radical, etc. are illustrated.

[0038] The compound expressed with the above-mentioned general formula ** is more specifically expressed with following general formula **, when the valence of transition metals is 4.

R1 a R2 b R3 c R4 d M ** (among formula **) M is a zirconium, titanium, or a hafnium and is R1. It is the ligand which has a cyclopentadienyl frame. R2 and R3 And R4 The ligand which has a cyclopentadienyl frame, it is alkyl group, cycloalkyl radical, aryl group, aralkyl radical, alkoxy group, aryloxy radical, halogen atom, trialkylsilyl group, and $-SO_3 R$ or a hydrogen atom, and a is one or more integers and is $a+b+c+d=4$.

[0039] In this invention, it sets to the above-mentioned general formula **, and is R2 and R3. And R4 The transition-metals compound which is the ligand in which one piece has a cyclopentadienyl frame inside, for example, R1, And the transition-metals compound which is the ligand in which R2 has a cyclopentadienyl frame is used preferably. The ligand which has these cyclopentadienyl frames An alkylidene radical; silylene radical or dimethyl silylenes, such as ethylene and a propylene, [, such as alkylene group; diphenylmethylenes] [, such as permutation alkylene group; isopropylidene] You may be combined through permutation silylene radicals; such as diphenyl silylene and methylphenyl silylene, etc. Moreover, R3 And R4 They are ligand [which has a cyclopentadienyl frame], alkyl group, cycloalkyl radical, aryl group, aralkyl radical, alkoxy group, aryloxy radical, halogen atom, trialkylsilyl group, and $SO_3 R$, or a hydrogen atom.

[0040] Below, M illustrates a compound concrete about the transition-metals compound which is a zirconium. Namely, for example, screw (cyclopentadienyl) zirconium dichloride, Screw (indenyl) zirconium jib ROMIDO screw (indenyl) zirconium dichloride -- Screw (indenyl) zirconium screw (p-toluene sulfonate) screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Screw (fluorenyl) zirconium dichloride, ethylene screw (cyclopentadienyl) zirconium dichloride, Ethylene screw (methylcyclopentadienyl) zirconium dichloride, Ethylene screw (dimethylcyclopentadienyl) zirconium dichloride, Ethylene screw (trimethylcyclopentadienyl) zirconium dichloride, Ethylene screw (tetramethylcyclopentadienyl) zirconium dichloride, Ethylene screw (indenyl) zirconium jib ROMIDO ethylene screw (indenyl) zirconium dichloride -- An ethylene screw (indenyl) dimethyl zirconium, an ethylene screw (indenyl) diphenyl zirconium, Ethylene screw (indenyl) methyl zirconium mono-chloride, an ethylene screw (indenyl) zirconium screw (methane sulfonate), An ethylene screw (indenyl) zirconium screw (p-toluene sulfonate), An ethylene screw (indenyl) zirconium screw (trifluoromethane sulfonate), Ethylene screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Isopropylidene (cyclo PENTA diphenyl-fluorenyl) zirconium dichloride, Isopropylidene (cyclopentadienyl-methylcyclopentadienyl) zirconium dichloride, Methylenebis (cyclopentadienyl) zirconium dichloride, methylenebis (methylcyclopentadienyl) zirconium dichloride, Methylenebis (dimethylcyclopentadienyl) zirconium dichloride, Methylenebis (trimethylcyclopentadienyl) zirconium dichloride, Methylenebis (tetramethylcyclopentadienyl) zirconium dichloride, Methylenebis (indenyl) zirconium dichloride, a methylenebis (indenyl) zirconium screw (trifluoromethane sulfonate), Methylenebis (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Methylene (cyclopentadienyl-fluorenyl) zirconium dichloride, Dimethyl silylene screw (cyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (methylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (dimethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (trimethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (tetramethylcyclopentadienyl) zirconium dichloride, Dimethyl silylene screw (indenyl) zirconium dichloride, a dimethyl silylene screw (indenyl) zirconium screw (trifluoromethane sulfonate), Dimethyl silylene screw (4, 5, 6, 7-tetrahydro indenyl) zirconium dichloride, Dimethyl silylene (cyclo PENTA diphenyl-fluorenyl) zirconium dichloride, Diphenyl

silylene screw (indenyl) zirconium dichloride, methylphenyl silylene screw (indenyl) zirconium dichloride, Screw (methylcyclopentadienyl) zirconium dichloride, screw (dimethylcyclopentadienyl) zirconium dichloride, Screw (dimethylcyclopentadienyl) zirconium ethoxy chloride, A screw (dimethylcyclopentadienyl) zirconium screw (trifluoromethane sulfonate), Screw (ethylcyclopentadienyl) zirconium dichloride, screw (methylethyl cyclopentadienyl) zirconium dichloride, A screw (pro PIRUSHI-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dichloride, -1, 2-ethane diyl titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene zirconium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Methylene zirconium dimethyl (the 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) methylene titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene zirconium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene titanium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene zirconium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) Isopropylidene titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dimethyl, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dichloride, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dichloride, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl zirconium dibenzyl, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dimethyl, (Methylamide) (tetramethyl-eta5-cyclopentadienyl) (Methylamide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, dimethyl (methylamide) (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, - (tetramethyl (ethyl amide)-eta5-cyclopentadienyl) methylene titanium dichloride, - methylene titanium dimethyl, (Ethyl amide) (tetramethyl-eta5-cyclopentadienyl) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, (The 3rd class butyl amide) Dibenzyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (The 3rd class butyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (Benzyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium diphenyl, (Benzyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, (Phenyl phosphide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (2-methoxyphenyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (4-fluoro phenyl amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) amide titanium dichloride, (2, 6-JI (1-methylethyl) phenyl) (amide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (4-methoxyphenyl amide) Dimethyl (1-methylethoxy) silane titanium trichloride, (Tetramethyl-eta5-cyclopentadienyl) 1-(the 3rd class butyl amide)-2-(tetramethyl-eta5-cyclopentadienyl)-1, 1 and 2, 2-tetramethyl disilane titanium dichloride, 1-(the 3rd class butyl amide)-2-(tetramethyl-eta5-cyclopentadienyl)-1, 1 and 2, 2-tetramethyl disilane zirconium dichloride, Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dimethyl, (The 3rd class butyl amide) Dimethyl (eta5-cyclopentadienyl) silane titanium dichloride, (The 3rd class butyl amide) Dimethyl (eta5-cyclopentadienyl) silane zirconium dichloride, (The 3rd class butyl amide) (Anilide) Dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, dimethyl (anilide) (tetramethyl-eta5-cyclopentadienyl) silane zirconium dichloride, etc. are illustrated.

[0041] In this invention, in order to manufacture the polymer which has desired physical properties, the transition-metals compound of the IVB group containing the ligand which has at least two sorts of [A] cyclopentadienyl frames is chosen, and it becomes possible to control the molecular weight of a polymer, a copolymer constituent, etc. by suitable selection to arbitration.

[0042] As a particle (b-1)-like inorganic solid-state of this invention A porosity inorganic solid-state is desirable. For example, SiO₂, aluminum 2O₃, MgO, MgCl₂, ZrO₂, TiO₂, B-2 O₃, CaO, ZnO, The mixture which is BaO, V₂ O₅, Cr 2O₃, ThO, etc., or contains these, Or they are these

multiple oxides, for example, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-aluminum } 2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr } 2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2\text{-MgO}$, etc. the inside of these — SiO_2 , aluminum 2O_3 , and MgO and MgCl_2 from — what uses at least one sort of components chosen from the becoming group as a principal component is desirable.

[0043] The particle-like inorganic solid-state of this invention has a hydroxyl group on a front face. In this invention, the hydroxyl group which a particle-like inorganic solid-state has on a front face is usually firmly held under polymerization conditions on a particle-like inorganic solid-state front face, and means the OH radical which generates H_2O with heating in an elevated temperature.

[0044] The method of obtaining the particle-like inorganic solid-state with which the hydroxyl group was firmly held on the front face under polymerization conditions is based on the approach of leaving a particle-like inorganic solid-state for 3 hours or more, for example under the temperature conditions as the time of a polymerization that it is the same in desiccation nitrogen, or the conditions of the temperature beyond it. The amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face in this invention is expressed by the rate (% of the weight) to the front [heating] particle-like inorganic solid-state weight of the weight decrement of this inorganic solid-state when heating a particle-like inorganic solid-state at 1000 degrees C under ordinary pressure.

[0045] As for the amount of the hydroxyl group which the particle-like inorganic solid-state of this invention has on a front face, it is desirable that it is the amount which commits effectively an organic (b-2) aluminum oxy compound in case a particle-like inorganic solid-state is supported. In this case, the alkyl group in an organic aluminum oxy compound being crushed with this hydroxyl group, and discovering the catalyst engine performance, if many [too] is checked to the amount of the organic aluminum oxy compound which the amount of this hydroxyl group uses. Moreover, to the organic aluminum oxy compound which the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face uses, if too few, trouble will be caused to support of an organic aluminum oxy compound. When there are too few amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face to an organic aluminum oxy compound, it becomes impossible that is, to support the organic aluminum oxy compound of a desired amount firmly on a particle-like inorganic solid-state front face, although it is thought that the hydroxyl group which a particle-like inorganic solid-state has on a front face reacts with the alkyl group of an organic aluminum oxy compound, and forms O-aluminum association.

[0046] An upper limit is one or less, the range of the mole ratio (OH/Alb -2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which a particle-like inorganic solid-state has on a front face in this invention is 0.7 or less preferably, a minimum is 0.01 or more and it is desirable that it is 0.05 or more preferably.

[0047] Moreover, in order to support the need and an effective quantity of an organic aluminum oxy compound to a polymerization, as for the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face, it is desirable that it is at least 0.5% of the weight or more of a particle-like inorganic solid-state, and it is desirable that it is 1 more % of the weight or more. However, if there are too many amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face, the inclination for activity to fall will be seen. Although it thinks because the reaction site of this with an organic aluminum oxy compound probably increases too much and the effectiveness as a co-catalyst of an organic aluminum oxy compound is restricted as a result, it is unknown for details. Thus, since there is an inclination for activity to fall when there are too many amounts of the hydroxyl group which a particle-like inorganic solid-state has on a front face, it is 10 % of the weight more preferably, and the amount of the upper limit of this hydroxyl group is 8 % of the weight still more preferably, and it is 12 % of the weight preferably, and desirable [an amount] that it is 6 % of the weight still more preferably.

[0048] In this invention, the amount of the hydroxyl group which a particle-like inorganic solid-state has on a front face can be adjusted by heating under suitable conditions if needed. In this invention, the hydroxyl group which a particle-like inorganic solid-state has on a front face can

also denaturalize by processing chemically with an organoaluminium compound etc. Thus, when a particle-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face with an organoaluminium compound, it is possible to adjust the amount of this hydroxyl group substantially, and (b-2) the effectiveness of reducing the amount of the organic aluminum oxy compound used is also found out.

[0049] As such an organoaluminium compound, the organoaluminium compound expressed with following general formula **, for example can be illustrated.

$R_5 \text{ n AlX}_3\text{-n} \dots **$ (R_5 is the hydrocarbon group of carbon numbers 1-12 among a formula, X is a halogen or hydrogen, and n is 1-3.) It sets to the above-mentioned general formula **, and is R_5 . Although it is the hydrocarbon group, for example, the alkyl group, cycloalkyl radical, or aryl group of carbon numbers 1-12 Specifically, they are a methyl group, an ethyl group, n-propyl group, an isopropyl group, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a cyclopentyl group, a cyclohexyl radical, a phenyl group, a tolyl group, etc.

[0050] As such an organoaluminium compound, the following compounds are specifically used. For example, trimethylaluminum, triethylaluminum, triisopropyl aluminum, Alkenyl aluminum, such as trialkylaluminum; isoprenyl aluminum, such as triisobutylaluminum, trioctyl aluminum, and Tri 2-ethylhexyl aluminum; Dimethyl aluminum chloride, a diethylaluminium chloride, Diisopropyl aluminum chloride, diisobutyl aluminum chloride, Dialkyl aluminum halide, such as dimethyl aluminum bromide; Methylaluminium sesquichloride, Ethylaluminium sesquichloride, isopropylaluminium sesquichloride, Alkylaluminium sesquihalide, such as butyl aluminum sesquichloride and ethylaluminiumsesquibromide; Methyl aluminum dichloride, Ethyl aluminum dichloride, isopropyl aluminum dichloride, ethyl aluminum -- a jib -- alkylaluminum dihalide [such as ROMIDO,]; -- they are dialkyl aluminum hydrides, such as a diethyl aluminum hydride and a diisobutyl aluminum hydride, etc.

[0051] In this invention, when a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face using the above-mentioned organoaluminium compound, the amount of this organic aluminum used is an amount from which the mole ratio (AlR/OH) to this hydroxyl group (OH) of the aluminum (AlR) in this organic aluminum becomes one or less.

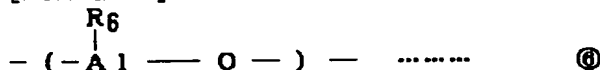
[0052] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face in this invention using the above-mentioned organoaluminium compound, Usually, (b-1) although this hydroxyl group is denaturalized by contacting an organoaluminium compound and a particle (b-1)-like inorganic solid-state before supporting an organic (b-2) aluminum oxy compound into a particle-like inorganic solid-state The denaturation of this hydroxyl group and support of an organic aluminum oxy compound may be performed to coincidence by mixing an organoaluminium compound and an organic (b-2) aluminum oxy compound beforehand, and contacting this mixture and a particle (b-1)-like inorganic solid-state after an appropriate time.

[0053] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face by this invention using the above-mentioned organoaluminium compound, it is considered that the aluminum in the mole ratio (OH/Alb -2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which said particle-like inorganic solid-state has on a front face is the value which added the aluminum (AlR) in this organoaluminium compound. Therefore, the upper limit said whose particle-like inorganic solid-state is the desirable range of the mole ratio (OH/Alb -2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which it has on a front face is one or less, and it is 0.7 or less preferably. The range which a minimum is 0.01 or more and is 0.05 or more preferably When a particle-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face using the above-mentioned organoaluminium compound In order that a particle-like inorganic solid-state may denaturalize the aluminum (Alb-2) and this hydroxyl group in the organic (b-2) aluminum oxy compound of the hydroxyl group (OH) which it has on a front face An upper limit is one or less, the desirable range of the mole ratio (OH/Alb-2+AlR) to the sum of the aluminum (AlR) in the organic aluminum to be used is 0.7 or less preferably, and a minimum is 0.01 or more and regards or more as 0.05 preferably.

[0054] When a particle (b-1)-like inorganic solid-state denaturalizes the hydroxyl group which it has on a front face in this invention using the above-mentioned organoaluminium compound, as for the mole ratio (AIR/Alb-2) to the aluminum (Alb-2) in the organic (b-2) aluminum oxy compound of the aluminum (AIR) in this organoaluminium compound, one or less is desirable. The organic aluminum oxy compound used by this invention (b-2) has the alkyloxy aluminum unit expressed with following type **.

[0055]

[Formula 1]



[0056] (R6 is the carbonization water machine of carbon numbers 1-12 among a formula.) It sets at an above-mentioned ceremony and is R6. A methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a decyl group, a cyclohexyl radical, a cyclo octyl radical, etc. can specifically be illustrated. A methyl group and an ethyl group are desirable in these, and especially a methyl group is desirable. In the above-mentioned formula, there are methylalumoxane, ethylalumoxane, n-propyl alumoxane, isopropyl alumoxane, n-buthylalumoxane, isobuthylalumoxane, pentyl alumoxane, hexyl alumoxane, octyl alumoxane, DESHIRU alumoxane, cyclohexyl alumoxane, cyclo octyl alumoxane, etc. as an example of the organic aluminum oxy compound which consists of one kind of alkylaluminum units. Methylalumoxane and ethylalumoxane are desirable in these and especially methylalumoxane is desirable. Thus, although the organic aluminum oxy compound of this invention is constituted per alkyloxy aluminum expressed with the above-mentioned formula **, it is not necessarily limited to the compound which consists of one kind of configuration unit, and may consist of two or more kinds of configuration units. For example, it is methylethyl alumoxane, methylpropyl alumoxane, methylbutyl alumoxane, etc., and the ratio of various configuration units can be taken to arbitration in 0 - 100% of range. Moreover, you may be the mixture of two or more kinds of organic aluminum oxy compounds which consists of one kind of configuration unit. For example, they are the mixture of methylalumoxane and ethylalumoxane, the mixture of methylalumoxane and n-propyl alumoxane, the mixture of methylalumoxane and isobuthylalumoxane, etc.

[0057] Moreover, the organic aluminum oxy compound of this invention may contain the unreacted chemical which comes from the manufacture approach. That is, generally, although an organic aluminum oxy compound is obtained by the reaction of trialkylaluminium and H₂O, some of these raw materials may remain as an unreacted chemical. For example, in composition of methylalumoxane, trimethylaluminum and H₂O are used as a raw material, but both these both [one of the two or] are the cases where it is contained in methylalumoxane as an unreacted chemical etc. In the manufacture approach of the organic aluminum oxy compound the above-mentioned instantiation, in order to usually use many trialkylaluminiums rather than H₂O, trialkylaluminium is contained in an organic aluminum oxy compound as a residual chemical in many cases.

[0058] As a [C] organoaluminium compound (it may be indicated as "component [C] below) used by this invention, the organoaluminium compound expressed with following general formula **, for example can be illustrated.

R₇ n AlX_{3-n} ** (R₇ is the hydrocarbon group of carbon numbers 1-12 among a formula, X is a halogen or hydrogen, and n is 1-3.) It sets to the above-mentioned general formula **, and is R₇. Although it is the hydrocarbon group, for example, the alkyl group, cycloalkyl radical, or aryl group of carbon numbers 1-12 Specifically, they are a methyl group, an ethyl group, n-propyl group, an isopropyl group, an isobutyl radical, a pentyl radical, a hexyl group, an octyl radical, a cyclopentyl group, a cyclohexyl radical, a phenyl group, a tolyl group, etc.

[0059] As such an organoaluminium compound, the following compounds are specifically used. Trimethylaluminum, triethylaluminum, triisopropyl aluminum, Alkenyl aluminum, such as trialkylaluminium; isoprenyl aluminum, such as triisobutylaluminum, trioctyl aluminum, and Tori 2-ethylhexyl aluminum; Dimethyl aluminum chloride, a diethylaluminium chloride, Diisopropyl

aluminum chloride, diisobutyl aluminum chloride, Dialkyl aluminum halide, such as dimethyl aluminum Promid; Methylaluminium sesquichloride, Ethylaluminium sesquichloride, isopropylaluminium sesquichloride, Alkylaluminium sesquihalide, such as butyl aluminum sesquichloride and ethyl aluminum sesquiPromid; Methyl aluminum dichloride, Ethyl aluminum dichloride, isopropyl aluminum dichloride, ethyl aluminum -- a jib -- alkylaluminum dihalide [, such as ROMIDO,]; -- alkylaluminum hydrides, such as a diethyl aluminum hydride and a diisobutyl aluminum hydride, etc.

[0060] Moreover, as a [C] organoaluminium compound, the compound expressed with following type ** can also be used.

R7 n AlY3-n ** (the inside of a formula, and R7 -- the above -- the same -- Y -OR8 radical --) - OSiR9 3 A radical and -OAlR102 A radical and -NR112 Radical, - SiR123 A radical or -N (R13) AlR142 It is a radical. n is 1-2. R8, R9, and R10 and R14 A methyl group, it is an ethyl group, an isopropyl group, an isobutyl radical, a cyclohexyl radical, a phenyl group, etc., R11 is hydrogen, a methyl group, an ethyl group, an isopropyl group, a phenyl group, a trimethylsilyl radical, etc., and R12 and R13 are a methyl group, an ethyl group, etc. Specifically as such an organoaluminium compound, the following compounds are used.

[0061] (i) R7 n aluminum(OR8)3-n The compound expressed, for example, a dimethyl aluminum methoxide, diethyl aluminum ethoxide, diisobutyl aluminum methoxide, etc.

(ii) R7 n aluminum(OSiR9 3)3-n The compound expressed, for example, Et2aluminum(OSiMe3) (iso-Bu)2 aluminum, (OSiMe3), 2 (iso-Bu) aluminum (OSiEt3), etc.

(iii) R7 n aluminum(OAlR102)3-n The compound 2 expressed, for example, Et2 AlOAlEt, and 2 (iso-Bu) AlOAl (iso-Bu)2 etc. .

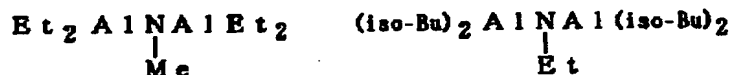
[0062] (iv) -- R7 n aluminum(NR112)3-n Compound 2 expressed, for example, Me2 AlNEt, Et2 AlNHMe, and Me2 AlNHET and Et2 AlN (SiMe3)2 and 2 (iso-Bu) AlN (SiMe3)2 etc. .

(v) -- R7 n aluminum(SiR123)3-n The compound 3 expressed, for example, 2 (iso-Bu) AlSiMe, etc. .

[0063]

[Formula 2]

(vi) $R_7^3 \text{Al} \begin{matrix} | \\ \text{R}^{13} \end{matrix} (\text{NAlR}^{14}_2)_3$ で表される化合物、例えば



[0064] In the organoaluminium compound expressed with above-mentioned general formula ** and **, they are R73aluminum and R7n aluminum(OR8)3-n and R7 n3(OAlR102)-n. The organoaluminium compound expressed can be mentioned as a suitable example, and it is R7. It is an isoalkyl group and especially the thing of n= 2 is desirable. Two or more sorts of these organoaluminium compounds can be mixed, and they can also use.

[0065] An IVB group's transition-metals compound with which the catalyst for olefin polymerization concerning this invention contains the ligand which has at least two sorts of [A] cyclopentadienyl frames (it may be indicated as "a component [A]" below), (b-1) Particle-like inorganic solid-state (it may be indicated as "a component (b-1)" below) Organic (b-2) aluminum oxy compound (it may be indicated as "a component (b-2)" below) [B] inorganic solid-state component which it comes to support (it may be indicated as "a component [B]" below) It consists of [C] organoaluminium compounds (it may be indicated as "a component [C]" below) if needed.

[0066] The configuration of the catalyst for olefin polymerization concerning this invention is shown in drawing 1 . As an approach of combining a component [C] two or more sorts of if needed [a component [A], a component [B], and if needed] by this invention For example, [whether a component [C] is respectively introduced directly independently into a polymerization system under polymerization conditions two or more sorts of if needed / a component [A], a component [B], and if needed / and] Or after mixing beforehand two or more

sorts of components [A], it is based on the approach of introducing a component [C] directly respectively into a polymerization system under polymerization conditions this component [A] mixture, a component [B], and if needed.

[0067] A component [B] can be adjusted by this invention by mixing a component (b-1) and a component (b-2) in an inert hydrocarbon catalyst. Specifically as this inert hydrocarbon medium, halogenated hydrocarbon or such mixture, such as aromatic hydrocarbon; ethylene chloride, such as alicyclic group hydrocarbon; benzene, such as aliphatic hydrocarbon; cyclopentanes, such as a propane, butane, a pentane, a hexane, a heptane, an octane, Deccan, a dodecane, and kerosene, a cyclohexane, and methylcyclopentane, toluene, and a xylene, chlorobenzene, and dichloromethane, etc. can be mentioned.

[0068] It faces mixing a component (b-1) and a component (b-2). A component (b-2) Per 1g (b-1) of components, Usually, it is desirable that it is the range of 10⁻³ to ten - two mols preferably 5x10⁻⁴ to 2xten - two mols, and, as for the concentration of a component (b-2), it is usually desirable for 5x10⁻²-5 mols /to be [l.] the range of 0.1-3 mols/l. preferably.

[0069] -50-150 degrees C of mixed temperature at the time of mixing a component (b-1) and a component (b-2) are usually -20-120 degrees C preferably. Since it is not necessary to keep it not necessarily constant [the temperature of this mixing] during mixing and the reaction of a component (b-1) and a component (b-2) is rather accompanied by generation of heat (for example, in order to suppress the temperature in early stages of mixing as low as possible and to complete a reaction further), it is desirable to control reaction temperature like making reaction temperature high at a mixed anaphase. In the case of the above-mentioned example, as desirable temperature in early stages of a reaction, it is -20-30 degrees C preferably, and 50-150-degree C -50-50 degrees C are usually 60-120 degrees C preferably as desirable temperature of a reaction anaphase. Moreover, the contact time of a component (b-1) and a component (b-2) is 1 - 50 hours preferably for 0.5 to 100 hours.

[0070] In this invention, although the activity of a catalyst becomes high and is so advantageous that the atomic ratio (Alb-2 / M) of the aluminum (Alb-2) in a component (b-2) and the transition metals (M) in all components [A] is large in cost, it is one side, and since the price [being general (b-2)] is high, if this atomic ratio is too high, cost will go up on the contrary. Therefore, the range of the atomic ratio (Alb-2 / M) of the aluminum in the component (b-2) of this invention, and the transition metals in all components [A] The upper limit is 2000 preferably and it is 1000 more preferably. It is 500 still more preferably, and is 300 still more preferably, and the minimum is ten or more preferably, it is 20 or more more preferably and it is recommended that they are 30 or more range still more preferably.

[0071] As for the atomic ratio (Alc/Alb -2) of the aluminum atom (Alc) in the component [C] used if needed, and the aluminum atom (Alb-2) in a component (b-2), it is usually desirable 0.01-3, and that it is the range of 0.03-1.5 preferably. As for the catalyst for olefin polymerization of this invention obtained as mentioned above, it is desirable per 1g (b-1) of components to support the aluminum atom of 5x10⁻⁴ - 5x10⁻² gram atom preferably about 10⁻⁴ to ten to 1 gram atom.

[0072] As an olefin which can carry out a polymerization according to such a catalyst for olefin polymerization The alpha olefin of 3-20, for example, a propylene, ethylene and a carbon number 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetra decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, cyclopentene, a cyclo heptene, Norbornene, 5-methyl-2-norbornene, tetracyclo dodecen, the 2-methyls 1, 4, and 5, 8-dimethano - 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene etc. can be mentioned. Furthermore, styrene, a vinyl cyclohexane, and dienes can also be used.

[0073] this invention -- a polymerization -- a suspension-polymerization method or a vapor-phase-polymerization method -- it can carry out also in any. The same thing as the inert hydrocarbon solvent used in the suspension-polymerization method on the occasion of component [B] adjustment can be used, and the olefin itself can also be used as a solvent. The range of -50-150 degrees C of polymerization temperature of the olefin using such a catalyst for olefin polymerization is usually 0-100 degrees C preferably. the polymerization preassure force - - usually -- ordinary pressure -100 kg/cm2 -- desirable -- ordinary pressure -50 kg/cm2 It is under a condition and a polymerization reaction can be performed also in which approach of a

batch process, half-continuous system, and continuous system.

[0074] The polymerization of this invention is performed using a multistage polymerization method. That is, a polymerization is performed by performing a polymerization gradually by letting it pass one by one to the curing units which arranged curing units in the serial and arranged the polymerization product in the middle of a catalyst component or/and a polymerization in this serial. In this invention, it can adjust depending on how of selection of a suitable component [A], the class of at least two sorts of components [A], and an amount to combine, and also the molecular weight of an olefin polymer can be adjusted by making hydrogen exist in a polymerization system, or changing polymerization temperature. In addition, in this invention, the catalyst for olefin polymerization can contain other useful components in olefin polymerization besides each above component.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these examples. In addition, in this invention, the physical properties of an ethylene system polymer are the following, and are made and measured.

[Consistency] The consistency in this invention was measured according to ASTM-D -1505.

[0076] [MI and HMI] MI and HMI in this invention are ASTM respectively. It is measured according to the conditions E in D1238, and Conditions F.

[Melting tension] It can ask for the melting tension (MT) in this invention by measuring the stress when extending the polymer which carried out melting with constant speed. In this invention, melting tension was measured using the Oriental energy machine factory melt tension measurement machine on conditions with a part for /, a resin temperature [of 190 degrees C], and part [for /] and diameter of 10-20mm nozzle in extrusion rate winding rate of 10mm 2.09mmphi, and a nozzle die length of 8mm. in addition -- the time of melting tension measurement -- a polymer -- beforehand -- as a thermostabilizer -- a 2 and 6-JI t butyl PARAKU resol -- 0.1wt(s)% -- it adds.

[0077] [Izod impact value] The Izod impact value in this invention is JIS. K The value for which 7110 can be asked according to the approach of a publication is said.

[ESCR] The environmental-stress-cracking-proof value (ESCR) in this invention is JIS. K According to 6760, it asks as 50% crack generating time amount in the approach of a constant strain environmental-stress-cracking trial.

[Dirt impact resistance value] A film with a thickness of 30 micrometers which formed membranes on the same membrane formation conditions is used for the dirt impact resistance value of this invention, and it is JIS. K 7124 was asked according to the approach of a publication.

[2% modulus] A film with a thickness of 30 micrometers which formed membranes on the same membrane formation conditions is used for 2% modulus in this invention, and it is JIS. K It asked by measuring a modulus value when distortion of a film reaches to 2% according to 7127.

[0078] (Example 1)

[Adjustment of a methylalumoxane support silica] Silica (pore volume of 1.10cm³ / g, and specific surface area are 318cm² / g, bulk density 0.38 g/cm³, and amount of surface water acid radicals 4.1wt%) 4.0g and toluene 40ml were put into 200ml glass flask which fully carried out the nitrogen purge, and it was made the letter of suspension, and cooled to -5 degrees C. Into this suspension, 30ml (Tosoh Akzo MMAO-3A, aluminum;1.15mol/l) of toluene solutions of methylalumoxane was dropped in 1 hour, keeping the temperature of suspension at -5 degrees C. Then, it performed at 0 degree C, the reaction was further performed under reflux conditions at the room temperature for 3 hours for 1 hour for 1 hour, it cooled to 20 degrees C after reaction termination, and the suspension of the silica which supported methylalumoxane was obtained.

[0079] [Polymerization] 0.80l. of hexanes was put into the autoclave made from stainless steel of 1.6l. of content volume which fully carried out the nitrogen purge, and 0.35 mols of 1-hexenes were added. After adding 0.5 millimols of silica suspension adjusted to this like the above by aluminum conversion, 15Nml addition of the hydrogen was carried out, ethylene was introduced

further, 7kg/cm² of total pressure was set to -G, and temperature in a system was made into 60 degrees C. 0.5 micromole of toluene solutions of screw (n-butylcyclopentadienyl) zirconium dichloride was added by zirconium conversion after that, temperature in a system was made into 70 degrees C, and the 1st step of polymerization was started. Then, the polymerization of eye this one stage was continued at 70 degrees C, having supplied ethylene and maintaining 7kg/cm² of total pressure at -G.

[0080] After [of the 1st step of polymerization initiation] 40 minutes, in order to perform the 2nd step of polymerization, after once purging the hydrogen in a polymerization system and newly adding the toluene solution of screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride into a 0.5 micromole polymerization system by zirconium conversion, the 2nd step of polymerization was started, having supplied ethylene again and having used 7kg/cm² of total pressure as -G. In this example, after newly adding screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride in a polymerization system, it considered as the 2nd step of polymerization. Then, after performing a polymerization for 20 minutes, the 2nd step of polymerization was ended. After it filtered the polymer after the 2nd step of polymerization termination and the methanol washed, one evening dried at 50 degrees C. In addition, adhesion of a polymer etc. was not accepted in the wall surface of a polymerization reactor. The operation conditions and polymerization result of this example 1 were shown in Table 1 and 2, respectively.

[0081] (Examples 2-6) the class of metallocene in each polymerization stage and its number of use classes, a comonomer, and the amount of hydrogenation -- polymerization time amount etc. was changed further, and also the polymerization of each stage was carried out like the example 7. The operation conditions and polymerization result of each example were shown in Table 1 and 2.

[0082] (Example 7)

[Adjustment of a methylalumoxane support silica] The suspension of the silica which carried out like the example 1 and supported methylalumoxane was obtained.

[Polymerization] After putting 0.80l. of hexanes into the autoclave made from stainless steel of 1.6l. of content volume which fully carried out the nitrogen purge, 0.5 millimols of silica suspension adjusted like the above were added by aluminum conversion. 15ml of hydrogen was added to this, ethylene was introduced further, 7kg/cm² of total pressure was set to -G, and temperature in a system was made into 60 degrees C. 0.5 micromole of toluene solutions of screw (n-butylcyclopentadienyl) zirconium dichloride was added by zirconium conversion after that, temperature in a system was immediately made into 70 degrees C, and the 1st step of polymerization was started.

[0083] The polymerization of eye this one stage was continued having supplied ethylene after that and maintaining 7kg/cm² of total pressure at -G. in order to perform the 2nd step of polymerization after [of polymerization initiation] 20 minutes -- the hydrogen in a polymerization system -- once -- purging -- new -- the toluene solution of screw (1, 2, 3, 4, 5-pentamethylcyclopentadienyl) zirconium dichloride -- zirconium conversion -- 0.5 micromole -- adding -- further -- after adding 0.10 mols of 1-hexenes, the 2nd step of polymerization was started, having supplied ethylene again and having used 7kg/cm² of total pressure as -G. Then, after performing a polymerization for 40 minutes, having supplied ethylene and maintaining 7kg/cm² of total pressure at -G, the polymerization of eye these two stages was ended.

[0084] After it filtered the polymer after polymerization termination and the methanol washed, one evening dried at 50 degrees C. In addition, adhesion of a polymer etc. was not accepted in the wall surface of a polymerization reactor. The operation conditions and polymerization result of this example 2 were shown in Table 1 and 3, respectively.

[0085] (Examples 8-10) the class of metallocene in each polymerization stage and its number of use classes, a comonomer, and the amount of hydrogenation -- polymerization time amount etc. was changed further, and also the polymerization of each stage was carried out like the example 7. The operation conditions and polymerization result of each example were shown in Table 1 and 2.

[0086] (Example 1 of a comparison) In the polymerization of an example 1, except having carried

out the 1st step of polymerization for 60 minutes, having used the addition of 0.35 mols and hydrogen as 15ml for the addition of 1-hexene, and having not carried out the 2nd more step of polymerization, a polymerization, after treatment, etc. were carried out in the same procedure as an example 1, and the polymer was obtained. These operation conditions and a polymerization result were shown in Table 1 and 2, respectively.

[0087] (Example 2 of a comparison) In the polymerization of an example 7, except having added 0.05 mols of 1-hexenes, having carried out the 1st step of polymerization for 60 minutes, and having not carried out the 2nd more step of polymerization, a polymerization, after treatment, etc. were carried out in the same procedure as an example 7, and the polymer was obtained. The operation condition and a polymerization result were shown in Table 1 and 3, respectively.

[0088]

[Table 1]

	MAO (mmol)	1 段 目				2 段 目				
		Zr 1 (μ mol)	1-ヘキセン (mol)	H ₂ (ml)	重合時間 (min)	Zr 2 (μ mol)	Zr 3 (μ mol)	1-ヘキセン (mol)	H ₂ (ml)	重合時間 (min)
実施例 1	0.5	A, 0.5	0.35	15	40	D, 0.5	—	—	—	20
実施例 2	0.5	A, 0.5	0.35	10	40	D, 0.5	—	—	—	20
実施例 3	0.5	D, 0.5	0	0	10	B, 0.5	—	0.35	3	50
実施例 4	0.5	E, 0.5	0	0	10	B, 0.5	—	0.35	3	50
実施例 5	0.5	E, 0.5	0	0	15	A, 0.25	B, 0.25	0.35	10	45
実施例 6	0.5	E, 0.5	0	0	15	A, 0.25	B, 0.25	0.15	10	45
比較例 1	0.5	A, 0.5	0.30	10	60	—	—	—	—	—
実施例 7	0.5	A, 0.5	0	15	20	D, 0.5	—	0.35	—	40
実施例 8	0.5	E, 0.5	0	0	15	A, 0.5	B, 0.5	0.05	15	45
実施例 9	0.5	B, 0.25	0	40	30	A, 0.75	—	0.05	0	30
実施例 10	0.5	B, 0.5	0.05	0	10	D, 0.5	—	0.0	10	50
比較例 2	0.5	A, 0.5	0.05	15	60	—	—	—	—	—

(注) A: ビス (n-ブチルシクロペンタジエニル) ジルコニウムジクロリド

B: エチレンビス (インデニル) ジルコニウムジクロリド

C: ビス (1, 3-ジメチルシクロペンタジエニル) ジルコニウムジクロリド

D: ビス (1, 2, 3, 4, 5-ペンタメチルシクロペンタジエニル) ジルコニウムジクロリド

E: ヒドロトリシバゾリルボレート (シクロペンタジエニル) ジルコニウムジクロリド

[0089]

[Table 2]

	MI (g/10min)	HMI (g/10min)	MIR	d (g/cm ³)	MT (g)	DIS (g)	2%モジュラス (kgf/cm ²)
実施例 1	1.5	52.7	35.1	0.921	7.1	1300	3100
実施例 2	1.1	33.6	30.5	0.915	8.5	1400	2000
実施例 3	1.0	32.0	32.0	0.908	9.1	1800	1550
実施例 4	0.92	28.7	31.2	0.902	8.7	>2000	1300
実施例 5	3.2	122.6	38.3	0.910	5.5	1580	1700
実施例 6	2.5	96.5	38.6	0.935	6.3	450	5700
比較例 1	1.5	0.14	15.1	0.924	2.2	600	2000

[0090]

[Table 3]

	M I (g/10min)	H M I (g/10min)	M I R	d (g/cm ³)	MT (g)	I z o d (kgf/cm/cm ²)	E S C R (h r)
実施例 7	0.44	16.5	37.5	0.953	24.5	35	> 1000
実施例 8	0.57	20.9	36.6	0.956	20.0	25	800
実施例 9	5.8	263	45.4	0.965	7.5	45	> 1000
実施例 10	0.35	19.4	38.3	0.959	27.8	41	> 1000
比較例 2	0.54	10.6	19.7	0.956	2.5		300

[Translation done.]

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- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing the configuration of the catalyst for olefin polymerization concerning this invention.

[Translation done.]

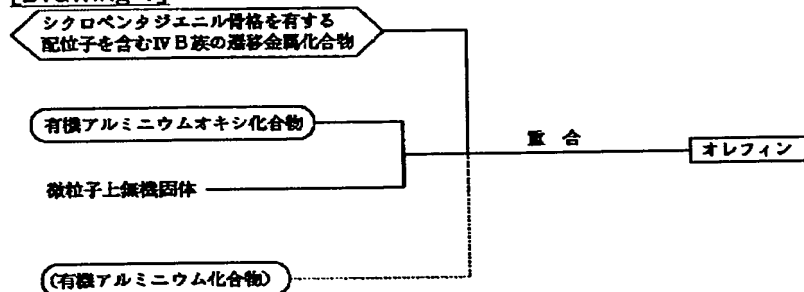
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DRAWINGS

[Drawing 1]



[Translation done.]